WASTE AND SECONDARY PRODUCT UTILIZATION IN HIGHWAY CONSTRUCTION

by

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Engineering

McMaster University
September 1975

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MASTER OF ENGINEERING (1975)
(Civil Engineering)

McMaster University,
Hamilton, Ontario,
Canada.

TITLE: Waste and Secondary Product Utilization in Highway Construction

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SUPERVISOR: Dr. John J. Emery

NUMBER OF PAGES: 256

SCOPE AND CONTENTS:

A satisfactory base stabilization process utilizing ground pelletized blast furnace slag as the cementing material has been developed. A number of aspects of pelletized slag base stabilization such as energy utilization, type of ground fines, catalysis effects, glass content, fly ash utilization, etc. are considered. The setting problems associated with the high lime content of steel slags in emulsified asphalt slurry seals were overcome by using blends of quick and slow set anionic emulsions. A large amount of information on waste and secondary product utilization is integrated throughout. Recommendations for future studies are given.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. John J. Emery and Mr. R.P. Cotsworth for their guidance during this research project, and particularly to Dr. Emery for his assistance and patience during the preparation of this thesis.

Financial support from the Department of Civil Engineering and Engineering Mechanics, McMaster University and National Slag Limited, Hamilton is gratefully acknowledged.

Special thanks are due to Mr. M. Forget and Mr. W. Sherriff for their assistance with the research facilities.

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1. INTRODUCTION

Wastes and secondary products generated by most human activity, particularly municipal, industrial and mining wastes, have often tended to pile up because of a lack of information on the wide potential for their utilization. The usually large difference between the quantities of wastes produced and the proportions utilized leads to environmental problems and the wasting of valuable resources through not considering their potential usefulness as structural or energy materials. Increasing concentrations of population and industry in rather restricted urban areas tend to involve complex and expensive waste management problems which will require new techniques to solve since landfill sites are becoming limited.

A systematic classification of wastes and a well-developed information exchange system on waste utilization seem critical since there is a great variety in the types and characteristics of wastes produced, and utilization technology is being developed by many researchers. Systematic classification of wastes enables a more effective management of wastes with regard to treatment and proper "disposal", and a well-organized information system on waste utilization provides data on utilization without needless duplication of research.

Among the various wastes, solid wastes such as slags from the iron and steel industry and some fly ashes from thermal power plants are presently of main interest in highway construction. Utilization of these wastes and secondary products in highway construction is one of their main outlets and is of primary interest to this thesis. Air-cooled blast furnace slags and steel slags are used as aggregates for base courses in highway pavements, in asphalt mixes and in slurry seals. Granulated or pelletized blast furnace slags are used as aggregates or cementing materials for granular base stabilization after some grinding of the pellets to take advantage of the cementitious properties of glassy pellets. It should be noted that utilization of these pellets as a cementing agent indicates the two general advantages of waste and secondary product utilization: firstly, the energy saving since the energy-intensive clinkering process of cement manufacture is eliminated; and secondly, utilizing the latent cementing properties of the granulated or pelletized blast furnace slag reduces the demand for natural resources while decreasing potential disposal problems.

The fly ash-lime-water system, and its pozzolanic reaction, were studied briefly for base stabilization applications using fly ash from Ontario Hydro's Lakeview power plant. The effects of glass content, fineness and chemical or mineralogical composition on strength development for both slag-cement and pozzolanic reactions in association with lime content, calcium chloride, and catalysis effects of portland cement on slag-cement base stabilization were investigated in detail. Autoclaving effects on stabilized base specimens and bricks made from slag fines were studied briefly. Slurry seal mixes made from steel slags rich in free lime, which normally causes serious setting problems in slurry seal construction, were examined for various emulsified asphalts and blends, and a suitable design determined.

In describing the research program, the necessary manufacturing process, and chemical or engineering properties of wastes and secondary products such as blast furnace slags, steel slags, fly ashes, pickle liquors, and commercial materials (lime, calcium chloride and emulsified asphalts) are discussed. Details are provided on the various cementing materials and the cementing mechanisms for portland cements and slag fines. These mechanisms are contrasted with pozzolanic reactions. Energy requirements in portland cement and slag cement manufacture are discussed to show the potential energy saving with slag cements.

The available literature has been widely used to guide these research activities.

2. GENERAL DESCRIPTIONS

2-1 WASTE

2-1-1 Definition of Waste

There is no universally accepted definition for waste, yet the concepts of waste recycling and utilization are among the most popular subjects of conversation and mass media treatment in society today. If one were pressed to define what is meant by waste, the most simple explanation would be: "Waste is anything that anybody throws away" [29]. Another more detailed definition would be: "Waste is any material which the owner considers will cost him more to keep than to discard" [69]. This second definition is starting to involve a few of the general concepts of waste management where disposal costs, material replacement costs, and many other factors are considered. Rather than adopting any complex definition and getting into waste management itself, in this thesis waste is simply considered to be anything thrown away.

In contrast, a secondary product is not really a waste, but is often viewed as such by the primary producer even when the potential nuisance becomes a money-making product.

2-1-2 Interaction of Materials - Energy - Environment

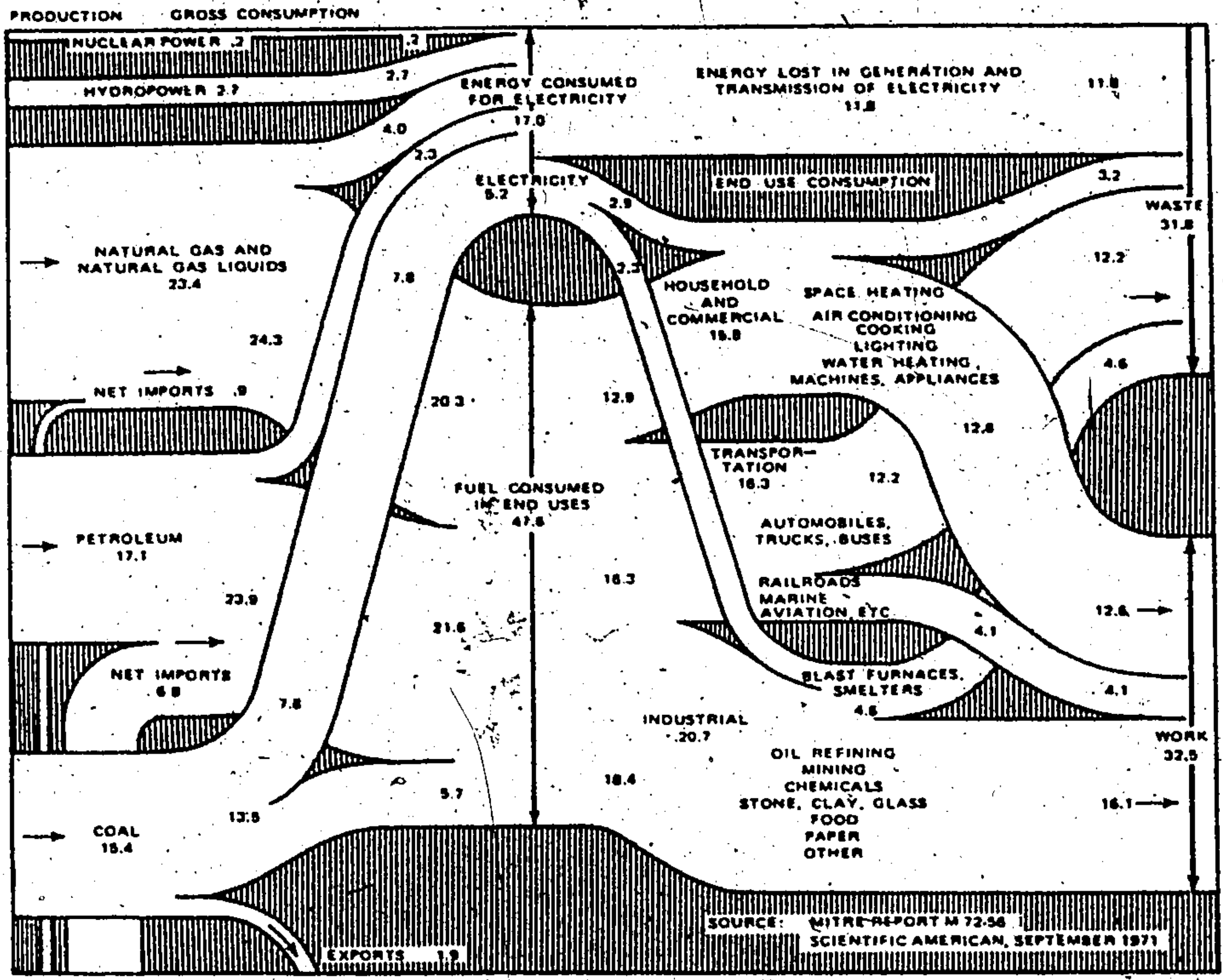
At present, it has been estimated that only 600 million people could be sustained on our earth if the per capita material and energy resource demands of each of them were the same as those for the average person in the United States [104]. Urgent shortages of certain key resources, particularly those related to the massive energy industry, have indicated the need for the closest possible co-operation between resource users and a wise management of the earth's stores. No part of the world community, whether a political or economic organization, can survive without a satisfactory distribution of local and global resources. This became apparent even to the relatively well resource-endowed North American continent at the end of 1973 with a sudden change in the smooth flow and sharing of petroleum, presently one of the most important earth resources.

While all life is dependent on the continual interaction of materials, energy and environment, only man has the power to make changes and must assume responsibility for the problems that arise. Man must question many old practices and uses of materials as it becomes obvious that there will be inadequate supplies, or distribution problems, in the near future as we try to maintain high standards of living.

What measures will or should we adopt to limit our consumption to assure an adequate materials supply to our community without significant damage to the environment? These problems have now become popular and the subject of much government action. For instance, in the United States, in order to conserve materials and minimize the wastage of useful resources, and still protect the environment, the Solid Waste Disposal Act (passed in 1965) was amended to the Resource Recovery Act, and the National Environmental Policy Act (NEPA) of 1970 was enacted [73]. In Canada, The Waste Management Act of 1970 was enacted along with The Fisheries Act, Canada Water Act, Ontario Water Resources Act, etc. to help control pollution and protect the environment.

Materials can be classified into two basic kinds, physical structure materials and energy materials. Energy materials are converted to energy and some parts of this energy is further used to produce both kinds of material. These processes all have some influence on the environment. As material shortages increase, more energy will be required to meet the demand from marginal or more remote sources. Then, as the energy demands rise, the demands on the environment also increase. Correspondingly, any hardening of environmental legislation (excluding conservation!) may also require greater energy requirements to produce the desired materials. All these aspects interact and cannot be treated independently. The recent energy crisis is probably just one symptom of the pending materials crisis - "the age of scarcity" - as man tries to find alternatives.

In the next three decades to the year 2000, it is predicted that the material requirements for the world will triple [12]. Yet, even with such future demands to face, the energy flow pattern shown in Figure 2-1 indicates that the amount of energy wasted in the United States is approximately equal to the amount put to use [12]. It is obvious that the efficient use and potential saving of energy resources is at least, or more important, than research on energy production. The decreased environmental costs are also evident. One of the more recent examples of efficient utilization of waste materials was demonstrated by the agreement to purchase 250,000 tons of Chicago City refuse annually for use as supplemental powerplant fuel by Chicago Commonwealth Edison Corporation [74]. Edison officials estimate that the garbage will substitute for



SOURCE: MITRE REPORT M 72-56
SCIENTIFIC AMERICAN, SEPTEMBER 1971

FIGURE 2-1 ENERGY FLOW CHART [12]

The Flow of Energy in the US System - The flow of energy through the US system in 1970, in quadrillions of Btu, is traced from fuels and other basic sources (left) to the conversion of energy into work for various industrial end products and waste heat (right). This graph originally appeared in *Scientific American*, Sept. 1971 and the MITRE Report M 72-56.

100,000 tons of coal or 13 million gallons of fuel oil per year with a cost of only $700,000 for the 250,000 tons of refuse. This garbage contains 77% combustible waste materials. Its equivalent heat energy is about two thousand billion Btu if it is assumed that the garbage contains 6000 Btu/lb of waste compared with coal at 10,000 Btu/lb and fuel oil at 144,000 Btu per U.S. gallon.

Another example is the recycling of aluminum cans manufactured from a material that has an original energy involvement of 8.45 Kwh plus 24,800 Btu per pound of molten aluminum. The effect on energy consumption in can manufacture of a 25% recycle of used cans is a reduction of 18% in electrical and 13% in thermal energy requirements. The energy requirements are reduced by one-half if a recycle of 60% of the cans produced is employed in conjunction with full utilization of customer-returned scrap [3]. Unfortunately, the total annual value of scrap now recovered including reclaimed metals, mineral materials, scrap iron, glass and other materials amounted to only 2 to 4 billion dollars in the United States in 1973 [12], compared to 300 billion dollars of materials produced.

2-1-3 Classification of Wastes

Concern for waste generation started with rapid industrialization and urbanization, which led to many of the current problems that remain to be solved. Previously, the management and classification of wastes was negligible. As solutions for industrial waste generation problems become more pressing, a systematic classification of wastes will be required so that problems and solutions can be related.

As in the case of defining wastes, a similar difficulty occurs in classifying wastes. One of the most broad and philosophical classifications used with the problem of solid-waste disposal [29] is that of avoidable and unavoidable wastes. The avoidable waste is the result of ignorance, carelessness or ineptitude, whereas unavoidable waste is the inevitable result of doing this or that job, no matter how well. Men can reduce their output of avoidable waste by learning to do a job "better", but they can only reduce their output of unavoidable waste by choosing not to do the job at all. Unfortunately, these classifications are too simplistic for most problems.

In *Waste Management and Public Health* [69], the wide range of wastes is classified into six major parts with regard to their sources, physical form, management and health hazards. This classification excludes sewage which is considered a particular waste since its generation is involuntary. The six categories are:

Municipal and industrial solid wastes;
Liquid industrial wastes;
Hazardous wastes;
Agricultural wastes and sewage sludge;
Abandoned automobiles; and
Litter.

In *Management of Industrial Waste in the Urban Region - A Classification System* [48], the classification system was developed to partially support a feasibility study of the U.S. Federal Environmental Protection Agency undertaking an inventory of industrial waste management, with a view to guiding national planning and policy formulation.

This classification system includes a list of 23 dimensions covering the essential components of an industrial waste classification system. This list is given in Table 2-1. In this extremely detailed classification system, physical form and material constituents in Exhibit A, and inventory coding Tables 1 and 3 in Exhibit B, are most concerned with the utilization of wastes.

2-1-4 Sources of Waste

A waste classification system based on the management of waste usually involves indicating the sources. The origin of a waste, with treatment or without treatment, and its routes to a final destination form the general flow of wastes. The treatment or further processing and beneficiation of particular wastes as they move from source to destination will be detailed later. The destination involves two basic choices - disposal or waste utilization (recycling, recovery), and is of prime importance here.

The source or origin of all wastes were grouped in *The Problem of Solid-Waste Disposal* [29]. This is reasonable since wastes other than solid-wastes will be generated at most locations and accompany the solid wastes adding further to disposal and/or recovery problems. A summary of these sources is shown in Table 2-2.

2-1-5 Solid Waste and Its Utilization

Solid waste is basically categorized by its physical form. This sort of bulk waste provides an obvious physical nuisance in our environment, whereas liquid and gaseous wastes cause different problems that

TABLE 2-1

WASTE CLASSIFICATION SYSTEM [48]

Exhibit A Dimensions of the Classification System

I. Recommended Dimensions for Industrial Waste Surveys

1. Geographic Locale (ZIP)	standard reference
2. Industrial Group Origin (SIC)	standard reference
3. Plant Boundary Reference	enters plant-generated and consumed within plant – leaves plant
4. Physical Form	Table 1* – inventory coding
5. Material Constituents	Table 3 – inventory coding
6. Chemical Composition	Tables 10 and 11 – inventory coding
7. Unit Process Origin	Table 4 – inventory coding
8. Treatment Process on Site	Table 4 – inventory coding
9. Method of Handling	Table 5 – inventory coding
10. Transportation Mode	Table 6 – inventory coding
11. Receiving Entity	Table 7 – inventory coding
12. Method of Final Disposal	Table 8 – inventory coding
13. Hazard Attributes	Table 9 – inventory coding
14. Information Content	plant and waste attributes included on the inventory form

II. Other Possible Survey Dimensions

15. Recyclability
16. Disposability
17. Mobility
18. Decomposibility
19. Toxicity
20. Other "Suitability" Indices

III. Special Dimensions for Library-Literature Acquisition Systems

21. Form of Publication or Accession	(book, scientific journal, proceedings, trade journal, government publication, industrial or private publication, university publication, magazine, newspaper, patent, brochure, etc.)
22. Information Type	(Bibliography, scientific research results, process evaluation, program evaluation, analytical methods, surveys, planning, policy, forecasts, legal aspects, economic aspects, community participation, environmental impact, etc.)
23. Relevance Dimension	(Hazards, Reuse & Recycling, Treatment, Disposal, Transportation, Collection, Storage, Waste Generation, Management and Administration, etc.)

*Tables refer to the Classification Tables of Exhibit B.

Exhibit B Classification Tables

Table 1 Physical Form of Batch

1. Solid
2. Semi-solids and Liquids – High Viscosity, e.g. Tars, Glues, Heavy Sludges, etc.
3. Slurries – Solid-Liquid Mixtures
4. Liquid – Low Viscosity, Flows in Pipes
5. Gas

Table 2 - Units Code

1. Tons*
2. Million Gallons*
3. Million Cubic Feet*
4. PPM (parts per million)

*(per day when reporting equipment capacity; per year when reporting material quantities)

Table 3 Waste Material Codes

10000	**Metals**
11000	**Ferrous Metals**
11100	**Largely Ferrous Bulk Scrap**
11101	Automobiles & Motorcycles
11102	Trucks
11103	Ships & Boats
11104	Airplanes
11105	Locomotives
11106	Engines & Motors
11107	Generators, Pumps, Turbines & Compressors
11108	Other Whole Machinery Units
11109	Freight Cars, Trailers, Barges and Other Mobile Units Without Machinery
11110	Tools, Dies, Machine Shop Equipment, etc.
11111	Storage Drums
11119	Other Large Bulk Largely Ferrous Scrap
11200	**Unplated Ferrous Materials & Alloys**
11211	Iron – All Grades
11212	Carbon Steel
11213	Stainless Steel
11214	Tungsten Steel
11215	Titanium Steel
11219	Other Steels and Ferrous Alloys
11300	**Plated Ferrous Materials**
11301	Chrome Plated
11302	Zinc Plated
11303	Tin Plated
11304	Nickel Plated
11305	Copper Plated
11306	Cadmium Plated
11319	Other Plated
12000	**Non-Ferrous Metals**
12100	**Independently Occuring Non-Ferrous**
12101	Aluminum
12102	Copper
12103	Lead
12104	Zinc
12105	Tin
12106	Nickel
12107	Mercury
12108	Silver
12109	Chromium
12110	Manganese
12111	Titanium
12112	Zirconium
12113	Gold
12114	Platinum
12115	Tungsten
12116	Cadmium
12117	Beryllium
12118	Tellurium
12119	Magnesium
12120	Molybdenum
12121	Palladium
12122	Selenium

TABLE 2-1 (Continued)

Table 3 (Continued)

12123	Silicon
12124	Boron
12125	Bismuth
12126	Cobalt
12127	Germanium
12128	Radium
12129	Uranium
12149	Other Non-Ferrous
12200	Non-Ferrous Alloys
12201	Brass
12202	Bronze
12203	Constantan
12204	Pewter
12205	Solder
12206	Babbitts
12207	Bismuth Alloy
12208	Monel
12219	Other Non-Ferrous Alloys
12300	Bulk & Composite Non-Ferrous Sources
12301	Largely Aluminum Machinery & Bodies
12302	Batteries
12303	Cables & Coverings
20000	Resins, Plastics & Rubbers
21000	Thermoplastic Resins
21001	Polyethylene-Low Density
21002	Polyethylene High Density
21003	Polyvinyl Chloride
21004	Polystyrene (Straight & Rubber Modified)
21005	Polypropylene
21006	Cellulosics
21019	Other Thermoplastic Resins
22000	Thermosetting Resins
22001	Phenolic
22002	Alkyd
22003	Polyester
22004	Urea & Melamine
22005	Coumarone-Indene
22006	Epoxy
22019	Other Thermosetting Resins
23000	Largely Rubber Products
23001	Tires
23002	Tire Tubes
23003	Foam & Sponge
23004	Sheet
23005	Hose
23006	Mechanical Goods
23019	Other Rubber
30000	Wood and Paper Materials
31000	Wood Products (Non-Paper)
31001	Natural Wood-Scraps, Sawdust, etc.
31002	Bark
31003	Pulp
31004	Leaves, Pine Cones, etc.
31005	Fiber Drums
31019	Other Wood Products
32000	Paper Products
32001	Pure Papers & Cardboards – Scraps, Cuttings, etc.
32002	Printed Paper Materials, Books, Magazines, etc.
32003	Wallboards -- Uncoated
32019	Other Paper Products
33000	Composite Papers, Cardboards & Wallboards
33001	Wax Coated
33002	Plastic Coated
33003	Oil & Asphaltic Coatings
33004	Aluminum Coated
33005	Carbon Coated
33006	Plaster Coated
33119	Other Coating & Composites
40000	Textiles & Related Fibres
41000	Natural Fibres
41001	Cotton
41002	Wool
41003	Silk
41004	Asbestos
41005	Glass
41006	Jute & Derivatives – Burlap, Rope, etc.
41007	Flax Waste
41008	Hemp Waste
41009	Worsted Waste
41010	Linters
41019	Other Natural Fibres
42000	Synthetic Fibres
42001	Rayon
42002	Nylon
42003	Polyesters – Dacron, Fortrel, Codel
42004	Polyacrylic – Orlon, Acrylan, Dynel, Creslan, Modacrylic
42019	Other Synthetic Fibres & Blends
43000	Composite Natural-Synthetic Fibres
43001	Largely Cotton
43002	Largely Wool
43003	Largely Rayon
43004	Largely Nylon
43005	Largely Polyesters
43006	Largely Polyacrylics
43019	Other Natural-Synthetic Composites
50000	Inert Materials
51000	Natural Geologic Origin
51001	Rocks, Gravels & Mine Tailings
51002	Sands
51003	Silts and Sediments
51004	Clays
51019	Other Natural Inerts
52000	Man Made Inerts
52100	Glass
52101	Clear
52102	Amber
52103	Green
52109	Other Colors
52200	Non-Glass Materials
52201	Ceramics
52202	Bricks
52203	Concrete & Cement
52204	Asphalts
52205	Plaster
52219	Other Non-Glass Inerts
52300	Industrial Process Inerts
52301	Slags
52302	Combustion Residues -- Heavy Ashes
52303	Combustion Residues – Fly Ash
52319	Other Industrial Process Inerts
53000	Miscellaneous Mixes: Rubble, Construction & Demolition Wastes
60000	Animal Product Wastes
61000	Animal Processing Wastes
61001	Tissues, Waste Viscera, etc.
61002	Fats & Derivatives
61003	Bone
61004	Shell
61005	Feathers
61006	Hair
61007	Unprocessed Skins & Hides
61008	Processed Skins, Hides & Leathers
61009	Wool Wastes-Lignin
61019	Other Animal Processing Wastes
62000	Dairy Wastes
63000	Live Animal Wastes – Raw Manures
63001	Cattle & Other Animal Manures
63002	Poultry & Other Fowl Manures
64000	Composts of Animal Waste
64001	From Cattle & Other Animal Manures
64002	From Poultry & Fowl Manures
64003	Other Animal Product Composts
65000	Dead Animals
70000	Vegetative Product Wastes (Except Wood)
70100	Edible Fruit & Vegetable Remains -- Putrescibles
70101	Shells (From Nuts, etc.)
70102	Stems, Leaves, Roots, Petals, etc.
70200	Coffee Grinds
70300	Fermentation and Culture Wastes
70400	Bagasse
70500	Sugars
70600	Vegetable Oils
70700	Vegetable Composts
70900	Other Vegetative Product Wastes
80000	Chemical & Biochemical Wastes
81000	Organic Chemicals
	See Table 10
82000	Inorganic Chemicals
	See Table 11
83000	General Chemical Process Wastes
83001	Inks
83002	Dyes
83003	Paints
83004	Adhesives
83005	Pharmaceutical Wastes
83006	Petrochemical Wastes
83007	Metal Treatment Wastes
83008	Solvents
83009	Waxes & Tars
83999	Other Organic or Inorganic Chemicals
84000	Conventional Treatment Process Sludges
84100	From Biological Sewage Treatment
84101	Raw Wet Sludge
84102	Digested Wet Sludge
84103	Dried Raw Sludge
84104	Dried Digested Sludge
84200	From Water Treatment & Conditioning Plants (Must be Chemically Classified)
84201	Wet Sludge
84202	Dried Sludge
85000	Waste Gases & Gas Borne Wastes
85001	Nitrogen
85002	Carbon Dioxide
85003	Carbon Monoxide
85004	Sulfur Oxides
85005	Nitrogen Oxides
85006	Hydrogen Sulfide
85007	Methane
85008	Aldehydes
85009	Lead
85010	Reactive Hydrocarbons
85011	Non-Reactive Hydrocarbons
85012	Particulates -- (gr/scfd 12% CO_2)
85013	Chemically Classified Components
90000	Miscellaneous Common Waste Mixtures (Waste Origin Implies A Characteristic Materials Mixture)
91000	Restaurant, Cafeteria & Kitchen Solid Waste Mixes
92000	Conventional Office Solid Wastes
93000	Supermarket, Grocery & Food Retail Solid Wastes
94000	Other Conventional Retail Establishment Solid Wastes
95000	Common Household-Municipal Solid Waste
95001	Segregated non-Putrescibles (Trash)
95002	Segregated Putrescibles (Garbage)
96000	Street & Yard Sweepings
97000	Wastes from Landscape & Garden Maintenance
98000	Composts of Mixed Municipal Type Wastes
99000	Sanitary Sewage & Wastewaters

TABLE 2-1 (Continued)

Table 4 Origin Processes (Including Treatment Processes)

1000	Operations Related to Plant's Product Management
1100	Basic Material Processing & Production (involves chemical treatment of input materials, e.g. extraction, oxidation, precipitation, heat treatment, plating, etc.)
1200	Product Manufacturing (involves shaping, forming, casting, extruding, cutting, binding, welding, sewing, etc.)
1300	Product Assembly or Disassembly
1400	Product Packaging (and Bottling), and Shipping
2000	Operations Related to Plant Facilities Services
2010	Receiving, Unpacking, and Warehousing Operations
2020	Plant Furnace, Steam & Boiler Operations
2030	Plant Intake-Water Treatment & Filtering
2040	Plant Laboratory
2050	Plant Restaurant or Cafeteria
2060	Interior Plant Maintenance & Cleaning
2070	Exterior Yard Maintenance & Cleaning
2080	Garage-Vehicle Maintenance and Service Area
2090	Offices
2100	Equipment Replacement
2200	Equipment Cleaning — Tank Washing, Rinsing, Etc.
3000	In-Plant Waste Treatment and Conversion Processes
3100	High Temperature Systems
3101	Controlled Air Incinerator
3102	Rotary Kiln Incinerator
3103	Catalytic Incinerator.
3104	Fluid Bed Incinerator
3105	High Temperature Slagging
3106	Open Pit & Teepee Incinerators
3107	Stoker Furnaces
3108	Batch Incinerator
3109	Fusion Torch Incinerator
3110	Partial Oxidation
3111	Pyrolysis
3119	Other High Temperature Systems
3200	Concentrated Waste Liquid and Sludge Systems
3201	Centrifuge
3202	Filtration
3203	Evaporation & Concentration
3204	Distillation
3205	Liquid-Liquid Extraction
3206	Biological Sludge & Oil Digestion
3219	Other Concentrated Waste Liquid Systems
3300	Dilute Waste Water Systems
3301	Settling Tanks (with or without precipitating agents)
3302	Neutralization
3303	Liquid-Liquid Separation (skimmers, gravity separators)
3304	Biological Oxidation — Lagoons
3305	Biological Oxidation — Trickling Filters
3306	Biological Oxidation — Aeration
3307	Biological Oxidation — Activated Sludge
3308	Activated Carbon Adsorption
3309	Ion Exchange Systems
3310	Interim Storage Lagoon
3319	Other Dilute Wastewater Systems
3400	Other Chemical Treatment
3401	Crystallization
3402	Reverse Osmosis
3403	Leaching
3404	Stripping
3405	Absorption
3406	Dialysis
3407	Electro-Dialysis
3408	Solvent Extraction
3409	Adsorption
3419	Other Liquid Treatment Systems
3500	Composting Systems
3501	Wind Row Composting
3502	Mechanical Composting
3600	Solid Separating Systems
3601	Magnetic Seperation
3602	Wet Process Material Seperation Systems.
3603	Dry Process Material Seperation Systems
3604	Optical Sorting Systems
3605	Manual Segregation of Material
3700	Waste Gas Treatment Systems
3701	Mechanical Collectors
3702	Electrostatic Precipitators
3703	Fabric Filters
3704	Wet Scrubbers
3705	Condensors
3706	Activated Carbon Adsorption
3719	Other Waste Gas Treatment
4000	Non-Plant Waste Sources
4100	Construction
4101.	Buildings
4102	Other Outdoor Facilities
4103	Roads & Rail
4104	Pipeline
4105	Dams & Reservoirs
4106	Canals & Ditches
4107	Dredging
4199	Other Construction
4200	Demolition
4201	Buildings & Houses
4202	Industrial Plants & Facilities
4299	Other Demolition
4300	Mining
4301	Strip Mining
4302	Deep Mining
4400	Agricultural
4401	Harvest & Farm Maintenance Operations
4402	Animal Ranching & Feeding
4500	Institutional Sources
4501	Hospitals & Nursing Homes
4502	Detention & Resident Centers (Jails, Orphanages, Etc.)
4503	Schools
4504	Libraries
4505	Zoos
4506	Aquaria
4507	Museums
4600	Miscellaneous Non-Plant Waste Sources
4601	Restaurants, Cafeterias and Kitchens
4602	Offices & Office Buildings
4603	Supermarkets, Groceries & Food Retail Establishments
4604	Other Retail Operations
4605	Households
4606	Municipal Street Cleaning & Maintenance
4607	Park & Garden Maintenance
5000	Storage & Transfer Facilities
5001	Waste Pile
5002	Conventional Cans & Drums
5003	Dumpster-Type Containers
5004	Sealed Containers
5005	Transfer Station

TABLE 2-1 (Continued)

Table 5 Handling Codes

01	Dewatered
02	Pulped
03	Unit Size Reduced (Milled, Shredded, Pulverized, etc.)
04	Sorted by Material (Segregated)
05	Sorted by Size
06	Compressed or Crushed
07	Baled
08	Containerized or Tanked
09	Washed
10	Disinfected
11	Moved Via Conveyor on Site
12	Moved Via Pipeline on Site
13	Moved Via Other Mechanism Such as Clamshell Bucket
14	Manually Handled

Table 6 Transportation Codes

01	Truck
02	Rail
03	Barge or Ship
04	Airplane
05	Direct Discharge to: Public Sewer
06	Direct Discharge to: River
07	Direct Discharge to: Lake or Reservoir
08	Direct Discharge to: Ocean
09	Direct Discharge to: Ground (Well Injection)
10	Airborne (e.g., Via Stack)
11	Remains on Site

Table 7 Delivery Entity Codes

01	Public Waste Agency – Municipal
02	Public Waste Agency – County
03	Public Waste Agency – Regional
04	Public Waste Agency – State
05	Public Waste Agency – Inter-State
06	Public Waste Agency – National
07	Public Waste Agency – International
08	Industrial or Cooperative Waste Association
09	Private Waste Disposal Contractor
10	Salvage Dealer
11	Other Industry
12	Self Disposal
13	Other

Table 8 Final Disposal Codes

01	Landfill or Dump	no intermediate treatment
02	Ocean Dump	
03	Other Water Dump	
04	Incinerate – Thermal Recovery	
05	Incinerate – No Thermal Recovery	
06	Pyrolize	
07	Hydrolize	
08	Compost or Digest	
09	Reuse or Recycle	
10	Treat as Sewage: Less than Primary	
11	Treat as Sewage: Primary	
12	Treat as Sewage: Secondary	
13	Treat As Sewage: Tertiary	
14	Treat as Sewage: Other	
15	Other Treatment Process	
16	Well Injection	
17	Deep Mine Disposal	
18	Stack to Atmosphere	
19	Other Disposal Method	
20	Irrigation or Soil Enrichment	

Table 9 Hazard Codes

(If Improperly Handled, Stored Or Disposed)

01	Explosive	
02	Radioactive	penetrating non-penetrating
03	Pathogenic	
04	Carcinogenic	
05	Mutagenic	
06	Teratogenic	
07	Corrosive	
08	Flammable	
09	Toxic To Humans Upon	: Inhalation
10		: Ingestion
11		: Contact.
12	Destructive Of Plant Or Animal Life In The Environment	
13	Otherwise Environmentally Dangerous If Improperly Handled Or Disposed	

Table 10 Organic Chemical Classification

81000	
81001	Saturated Aliphatic Hydrocarbons
81002	Unsaturated Aliphatic Hydrocarbons
81003	Cyclic Hydrocarbons
81004	Aromatic Hydrocarbons
81005	Heterocyclic Hydrocarbons – O
81006	Heterocyclic Hydrocarbons – S
81007	Heterocyclic Hydrocarbons – N (Except 81032 & 81033)
81008	Substituted Aliphatic Hydrocarbons – Sulfonated
81009	Substituted Aliphatic Hydrocarbons – Halogenated
81010	Substituted Aliphatic Hydrocarbons – Nitrated
81011	Substituted Aromatic Hydrocarbons – Sulfonated
81012	Substituted Aromatic Hydrocarbons – Halogenated
81013	Substituted Aromatic Hydrocarbons – Nitrated

Table 10 Organic Chemical Classification (Continued)

81014	Alcohols
81015	Polyhydroxyl Compounds
81016	Aldehydes
81017	Aliphatic Carboxylic Acids (n<5)
81018	Aliphatic Carboxylic Acids (n>5)
81019	Aromatic Carboxylic Acids
81020	Resin Acids
81021	Aliphatic Ketones
81022	Aromatic Ketones
81023	Aliphatic Esters
81024	Aromatic Esters
81025	Aliphatic Ethers
81026	Aromatic Ethers
81027	Sulfides
81028	Mercaptans
81029	Phenols
81030	Aliphatic Amines & Their Salts (Except 81041)
81031	Anilines
81032	Amides
81033	Pyridines
81034	Alkaloids
81035	Cyanides
81036	Isocyanates
81037	Sterols
81038	Carbohydrates
81039	Organometallic Compounds
81040	Salts – Organic Anion
81041	Salts – Organic Cation
81042	Carboxylic Acid Anhydrides
81043	Nitriles
81044	Peroxides

Table 11 Inorganic Chemical Classification

82 000 00

3rd and 4th digits – Atomic number of cation and/or more electropositive element
5th digit 0-unless oxy-cation then use 1 (at no. of metal in 3rd and 4th digits) –
0-unless mixed cation salt then use 2 (lower at no. metal in 3rd and 4th digit)
6th and 7th digit

01	Hydrides
02	Hydroxides
03	Borides
04	Borates
05	Carbides
06	Carbonates and bicarbonates
07	Nitrides
08	Azides
09	Cyanides
10	Thiocyanates
11	Ferro (II) cyanides
12	Amides
13	Nitrites
14	Nitrates
15	Oxides
16	Sulfides
17	Bisulfides
18	Sulfides and bisulfites
19	Sulfates and bisulfates
20	Fluorides
21	Fluorine oxy-anions
22	Aluminates
23	Silicides
24	Silicates
25	Phosphates
26	Phosphates (all)
27	Chlorides
28	Chlorine oxy-anions
29	Titanate
30	Vanadate
31	Chromium oxy-anions
32	Manganese oxy-anions
33	Zincates
34	Arsenides
35	Arsenic oxy-anions
36	Selenides or tellurides
37	Selenium or tellurium oxy-anions
38	Bromide and Iodide
39	Bromine and iodine oxy-anions
40-92	For other metal oxy-anions for at.no. >40 use at.no. of metal for example, 74 tungstate
93	Metal halo-anions
94	Miscellaneous

TABLE 2-2

SOURCES OF WASTE [29]

SOURCE	DESCRIPTION
Residential	Single family, multi family
Commercial	Hotels, schools, offices, restaurants, stores, auto services
Industrial	Natural resources, manufacturing, processing, assembly, distributing
Governmental	Streets, utilities, medical facilities, public bodies, parks and forests, highways, military operations
Agricultural	Animals (rearing and processing), plants (culture and processing)

may not be as obvious, but are often far more insidious. As a guideline, the classification of solid wastes from *The Problem of Solid-Waste Disposal* [29] is given in Table 2-3.

Fortunately, technology often exists for converting these solid waste nuisances into valuable resources or directly replacing resources ("Watts from Wastes" for instance). The objective of solid waste management should be, and usually is, to maximize the utilization of this potential resource and minimize environmental effects. Obviously, a better understanding of the properties of the various types of solid waste and the opportunities for changeability and association with commercial materials can maximize the efficient usage of such wastes. The wastes given in the inventory classification based on material constituents in Table 2-1, except codes 60000, 70000, 80000 and some of 90000, are well sorted into solid waste types.

From the many kinds of solid waste and secondary products available, slags from the iron and steel industry, fly ash from thermal power plants and pickle liquors (actually a liquid waste) from steel treating processes will be described in particular detail. These items are produced in large volumes in Ontario and are finding increasing utilization in construction. Commercial products such as lime, calcium chloride and asphalt are also described, since they are often required in the utilization of particular wastes as construction materials. It is hoped that the approach adopted in examining some specific wastes will indicate the general methodology adopted in the Highway Materials Laboratory.

TABLE 2-3

TYPES OF SOLID WASTE [29]

TYPE	DESCRIPTION	TYPE	DESCRIPTION
Industrial	organics inorganic residue hazardous materials hazardous and toxic chemicals wood and paper	Mining and Minerals	slag tailings culm
		Garbage	food residue food preparation spoilage
Agricultural	small and large animals process residue crop residue fertilizers pesticides animal manure erodable soil	Junk Vehicles and appliances	abandoned vehicles white-metal products
		Special Wastes	bulky products sewage residue small animals street sweepings pollution control residue pathological residue radioisotopes construction and demolition debris
Rubbish	paper glass metals plastic and rubber rags and clothes process residue yard trimmings wood		

2-2 MATERIAL DESCRIPTIONS

2-2-1 Waste and Secondary Product (By-products) Descriptions

2-2-1-1 Blast Furnace Slag

Many publications concerned with slag have been prepared by marketing organizations and individual researchers. Before presenting a description of blast furnace and steel slags, a general classification of the various slags produced in metal refining will be indicated. Slags are the non-metallic by-products which are obtained during the refining of metals (reduction and separation) from metallic ores, fluxing media and fuel. A general classification chart for slags is given in Figure 2-2.

The following discussion is largely concerned with blast furnace and steel slags from iron and steel production. Blast furnace and steel slags are the types of slag that presently find widest utilization.

Manufacture of Blast Furnace Slag

Blast furnace slag is defined in ASTM Designation C-125-71 as "the non-metallic product, consisting essentially of silicates and alumino silicates of lime and other bases, which is developed in a molten condition simultaneously with iron in a blast furnace". The iron ore, which is a mixture of oxides of iron, silica, and alumina, is introduced into the furnace with the calcium of the fluxing stone (limestone and/or dolomite), along with coke. The high temperature produced by the burning coke induces the chemical reaction of reduction

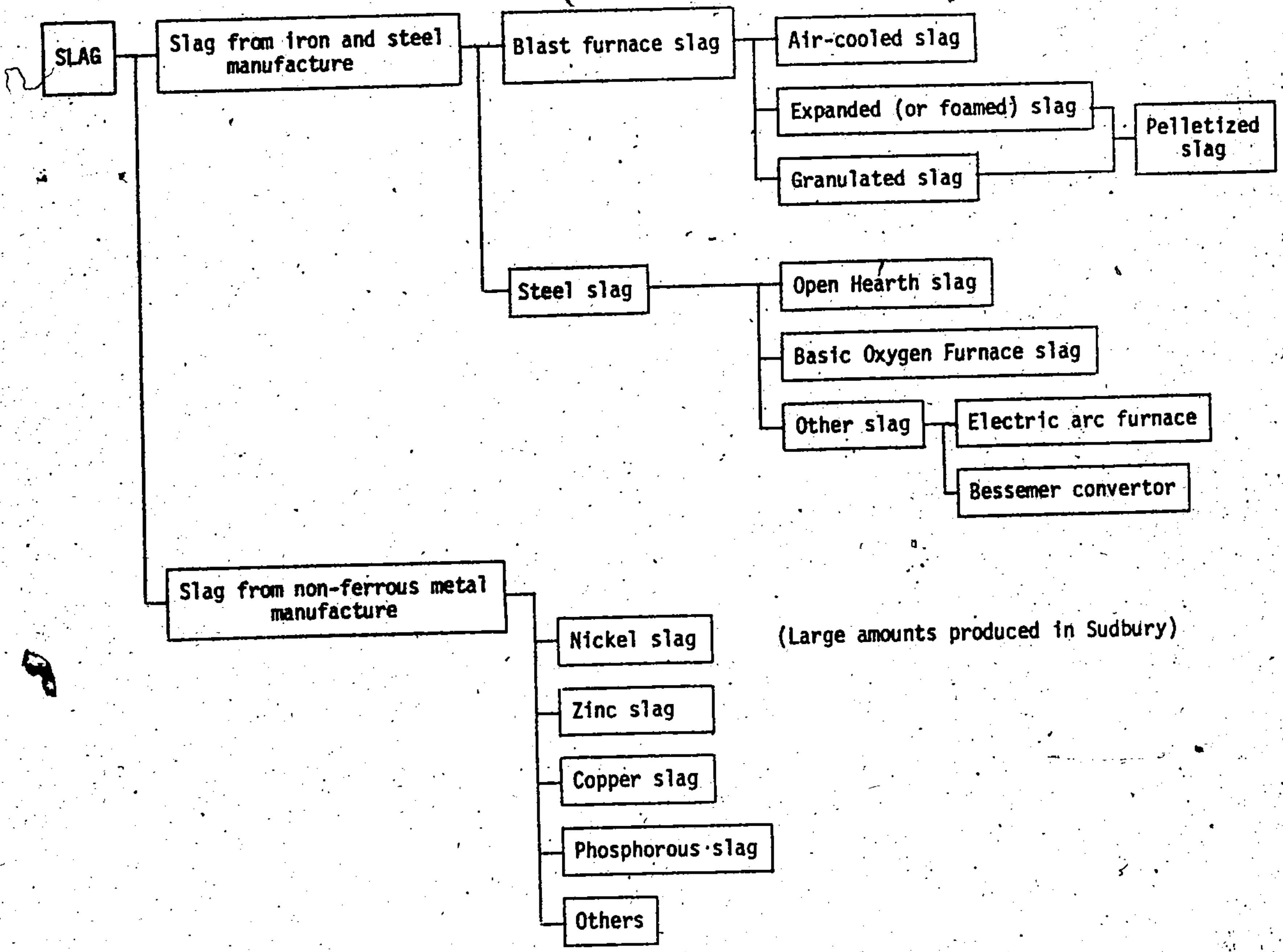


FIGURE 2-2 GENERAL CLASSIFICATION CHART FOR SLAG

and results in a separation of iron with the molten slag floating on top of the liquid iron at the bottom part of the furnace. (From 0.3 to 1.0 tons of slag per ton of iron produced depending on the ore, etc. [43] Figures as low as 0.2 tons of slag per ton of iron produced appear possible with de-sulphurization.)

Blast furnace operations are a continuous process, the raw materials being fed in at the top, and molten iron and slag being removed separately at the bottom part of the furnace. Figure 2-3 shows a schematic diagram for the production of slag during the blast furnace process.

The chemical composition of the blast furnace slag, as well as the quality of pig iron produced, is mainly controlled by the amount and properties of fluxing stone, provided other factors remain constant. Fluxing stone (limestone and/or dolomite) disassociates into calcium and magnesium oxides (CaO, MgO) and carbon dioxide (CO_2) when heated. These calcium and magnesium oxides react with the silica, alumina and minor impurities in the ore to form the slag. The other important function of fluxing stone is to combine with the sulphur that comes from the coke and gives the sulphurous smell often associated with blast furnace slags. A uniform mixture of ore, fluxing stone and coke is required to produce a consistent quality of pig iron and generally ensures a corresponding degree of uniformity in the quality of the slag. Lack of uniformity can be a significant problem in slag cement production and other special usages of blast furnace slag. If the chemical composition remains the same, the density, porosity and mineralogical composition of blast furnace slags will only be affected by

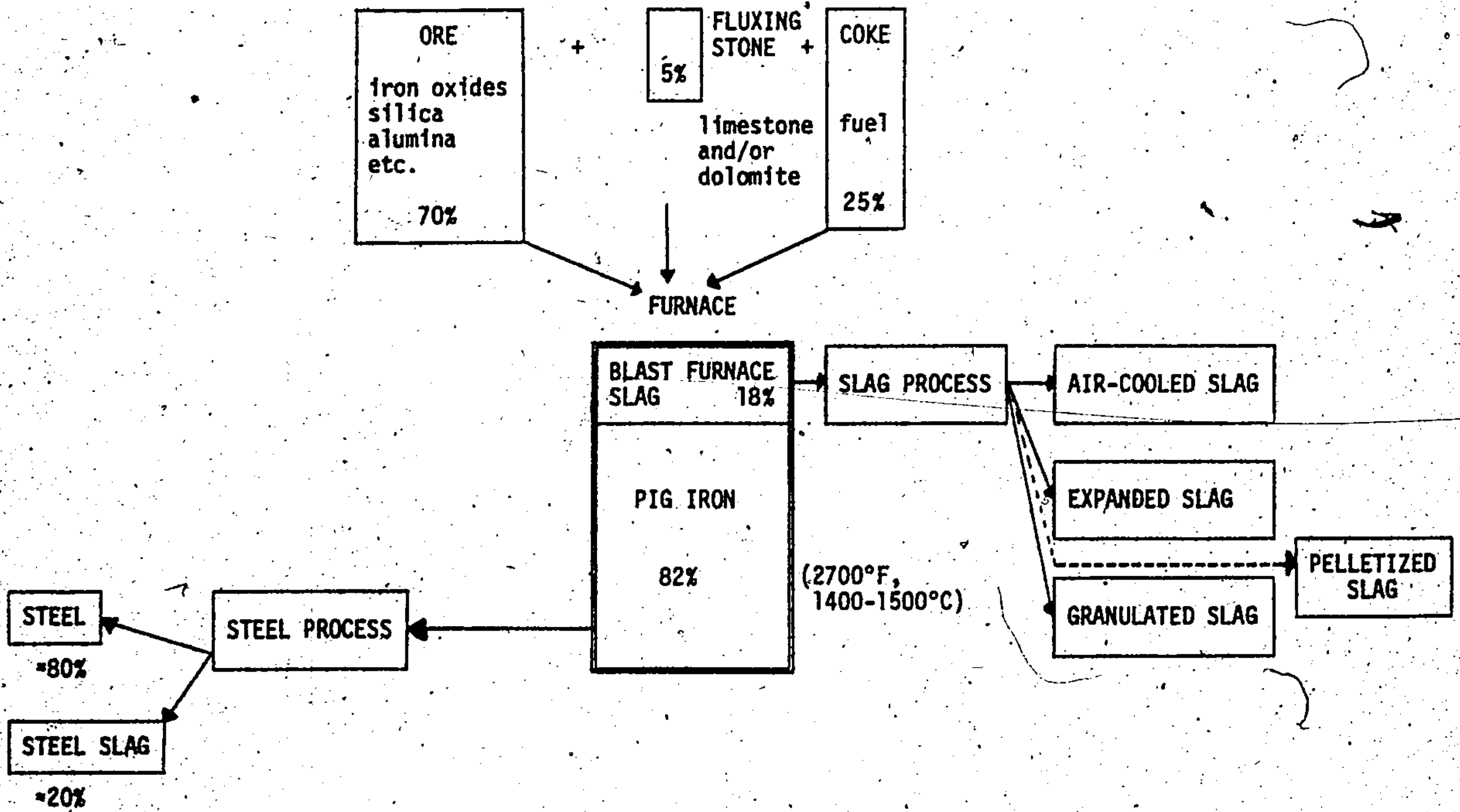


FIGURE 2-3 IRON AND BLAST FURNACE SLAG PROCESSES [81]
Percentages shown by weight

the processes involved in cooling the slag after it leaves the notch at the bottom of the blast furnace.

Blast furnace slag is classified into three main types: air-cooled, expanded or foamed, and granulated - depending upon the method of cooling from the molten state. It should be noted that pelletized slag is a product categorized between expanded slag and granulated slag because of the physical and mineralogical properties related to its pellet and glassy nature, respectively.

Air-Cooled Slag

Air-cooled blast furnace slag is allowed to solidify under atmospheric conditions, either in the ladle or in a pit, at a temperature of about 1400 to 1500°C [43]. During cooling, it develops a crystalline structure similar to that of a natural igneous rock. Crystallization takes place while the slag is cooling, beginning when the temperature of the slag drops to a point where the first mineral can form in a melt of that specific composition (around 1450°C) and ceasing when the melt solidifies. Crystals range from submicroscopic size to occasional crystals as large as 1/4 inch long [38,44].

Expanded Slag

Expanding of blast furnace slag was first carried out by Carl Schol in Germany in 1911 for use as lightweight aggregates [31]. The foaming process used in the U.K. for expanding blast furnace slag since 1935 is based on a British patent and utilizes the heat present in the molten slag [31]. The basic idea is that if water is blown under controlled conditions into the molten slag as it is tipped into a special pit, the sudden generation of steam will produce the desired expanded product. This foaming process is capable of producing lightweight aggregate from slags over a wide range of composition. The "falling" effect of slags rich in lime can be eliminated in this case since the formation of crystalline β dicalcium silicate, which may be metastable and might undergo a structural transformation from the β to the stable γ form is eliminated. (This transformation is accompanied by a 10% volume increase which can lead to spontaneous disintegration or "falling" [31,43,44,55]). Impurities present in the solid solution tend to stabilize the β dicalcium silicate polymorph [21]. Emphasis on the study of this dicalcium silicate, and the problem of slag stability and its relationship to the soundness of slag cements appears mainly in British slag investigations [31].

The expansion process should result in the molten slag crystallizing and also expanding to a light foamed product suitable for lightweight aggregates. This is in contrast to the granulating process discussed in the next section which should change the molten slag into solid glassy products which are generally undesirable as structural aggregates, but desirable for slag cement manufacture.

Granulated Slag

Granulated slag may be defined as the glassy, granular product formed when molten slag is suddenly chilled by immersion in water or by other methods such as high pressure water jets. In these cooling processes, crystals have no time to form and the slag is solidified as a glassy type material. The physical effect of these rapid cooling processes is for the slag to break up into porous particles ("slag sand"). Granulation also has certain chemical effects, highly important in producing cementitious materials (slag cement), that are discussed in detail later. There are three general methods of granulating slag [18, 22, 38]:

a) Pit process - Molten slag is introduced into a water pit.

b) Jet process - This is a modification of the pit process and the stream of molten slag is broken up by a high pressure water jet.

c) Dry granulation process - Using a mechanical device, the stream of molten slag is granulated into small particles by impact, and then sufficient water ~~for~~ quenching is fed in with the molten slag. The heat evaporates most of the residual water and leaves a relatively dry product.

The effect of the process is found to vary with the temperature of the water; the amount of water used; and, its method of application. The pit and jet processes are discussed in Reference 22 in some detail. A je[illegible] process was used at one time in slag-cement plants in the Middlesborough District of England in which the slag was blown into fine threads similar to the process generally used in the manufacture of mineral and glass wool. From an economic point of view, this method has the advantage of easy pulverization by the grinding machinery. However, this method has generally been superseded by the pit process that is presently used at most slag-cement plants. The pit process is often modified by the use of a jet of water playing on the slag before it strikes the trough containing the rapidly flowing stream of cooling water (trough-pit method). Other minor modifications are found in granulating plants based on local experience or particular handling problems.

The properties of expanded blast furnace slag are different from those of granulated blast furnace slag. These properties are related to the desired end use and are achieved by different methods of cooling the slag from the molten state. Expanded lightweight slag is formed when molten slag is expanded by applying a limited amount of water, or controlled quantity of water, and air or steam in order to expand the slag to a clinker without granulation. This chilling with a controlled amount of water, applied in such a way as to trap the steam in the mass, gives a porous product of pumice-like character. Cooling of the slag with a large excess of water produces granulated slag.

This expansion mechanism is quite similar to the production of expanded lightweight clays and shales, which expand or bloat to as much as seven times their original volume, owing to the formation of gas within the mass of the material at the fusion temperature or semi-plastic stage, often termed "the point of incipient vitrification". In the case of clay and shale expansion, they should contain mineral constituents which will produce gases at the softening temperature. If such mineral constituents are not naturally present in the clay, they may be introduced during the process.

However, molten slag has no constituent which produces foaming gases. Foaming is achieved by jetting or watering processes, and mechanical processes. Generally the amount of water used under controlled conditions is less than that required for granulation. Some portion of expanded slag may contain glassy material which is undesirable since granulation may occur during the cooling.

The chemical composition of the original molten slag may affect the expansion efficiency and quality of expanded products in terms of vitrification, as well as viscosity of the molten slag. Crystallization proceeds rather slowly in slags high in silica and more rapidly and completely in those high in lime and magnesia. That is, siliceous slags cool to glasses most easily while those of high lime content are more difficult to prevent from crystallizing. Viscosity decreases with increasing lime content and the viscosity of the silicate, near the freezing point, is so large that rearrangement of ions to form crystallization takes place slowly. However, no general relation exists between viscosity and composition as expressed in component oxides.

The chemical analysis of foamed slag is not very different from that of the original molten slag except that the sulphur content is somewhat lower, due to the reaction of the sulphides with water and liberation of sulphur gases. However, the mineralogical composition may suffer considerable change during the transition from liquid to solid, due to the conditions of cooling.

The foaming removes unsoundness in almost all slags. There seem to be slags which when air-cooled may fall or suffer spontaneous disintegration by structural transformation from the metastable β to the stable γ form. As blast furnace slag is made by the fusion of constituents which will tend to be variable even in strictly controlled processes, followed by cooling under more or less controlled conditions, the final product may have a wide range of compositions. Both the chemical and mineralogical compositions of blast furnace slag affect its physical properties. The compositions have been studied in considerable detail by producers, processors and users of blast furnace slag. Blast furnace slag is found to contain four major oxides - silica, alumina, lime, and magnesia - which constitute about 95% of the total. Minor constituents include sulphur, manganese, and iron, with traces of many other elements and components.

The raw materials (ores, fluxes, coke, etc.), the grade of metal being made, and differences in operating practice all influence the final chemical composition of slag. The silica-alumina ratio in the slag is fixed primarily by the ores selected and is approximately 3:1 by weight. The lime-magnesia ratio is controlled by the fluxing stone selected. The ratio of acids (SiO_2, $A\ell_2O_3$) to bases (CaO, MgO) normally approximates 1:1. This ratio is controlled by the operator increasing or decreasing the quantity of fluxing stone to produce the particular grade of iron desired as measured by silica and sulphur content. The chemical analysis of a typical blast furnace slag falls within the range shown in Table 2-4.

TABLE 2-4

TYPICAL CHEMICAL ANALYSIS OF BLAST FURNACE AND STEEL SLAGS [79]

CONSTITUENTS		BLAST FURNACE SLAG %	STEEL SLAG % (b)
Silica	SiO_2	33-42	15.6
Lime	CaO	36-45	41.3
Alumina	$A\ell_2O_3$	10-16	2.2
Magnesia	MgO	3-16	6.9
Sulphur (a)	S or SO_3	1-3	...
Iron Oxide	FeO, Fe_2O_3	0.3-2	20.0
Manganese Oxide	MnO	0.2-1.5	8.9

(a) principally in the form of calcium sulphide CaS

(b) BOF steel slag by Stelco Research and Development Department

Mineralogical Composition

The mineralogical composition of blast furnace slag plays an important part in determining its behaviour when used as a structural building material where a crystalline slag is desirable. It is of less direct interest for slag in the glassy or granulated form that is used mainly in slag cement manufacture. As indicated earlier, formation of crystals in slag depends largely on the rate of cooling, whereas the characteristics of the minerals depend primarily on the chemical composition. The most common mineral in a crystalline blast furnace slag is melilite - the solid solution series akermanite - gehlenite [3]. In blast furnace slags of low lime and high alumina content, the mineral anorthite may be detected, while in blast furnace slags of high lime content dicalcium silicate may be formed. Minor components are calcium sulphide, iron, alkalis and manganese oxides. A list of the many minerals that have been considered to occur in blast furnace slag is shown in Table 2-5 with the name, formula and mineral properties of some indicated.

The quaternary system of the four major constituents, CaO, SiO_2, Al_2O_3, and MgO, has not been studied thoroughly. The probable assemblages of minerals comprising the quaternary system cannot be predicted with certainty, but some estimations are very close to the results of miscroscopic studies. Lea [43] set out some possible assemblages as shown in Table 2-6, the upper parts showing the number of blast furnace slags out of a group of 21 from different iron works with that particular assemblage, the lower parts being some other assemblages that seem possible.

TABLE 2-5

CRYSTALLINE COMPOUNDS OF MINERALS IN BLAST FURNACE SLAG

NAME (1)	NAME (2)	MINERAL PROPERTIES (3) SYSTEM	MINERAL PROPERTIES (4) HABIT	(5) FORMULA	SHORT FORM (6) LEA	(7) REMARKS	(8) OBSERVER
Melilite series (solid solution)	Gehlenite	tetrogonal	short square prisms	$2CaOA\ell_2O_3SiO_2$	C_2AS	most common mineral silica	McCottery, Lord Guttman, Parker Ryder, Brown
	Akermanite			$2CaOMgO2SiO_2$	C_2MS_2	isomorphous mixture	
Monocalcium silicate	Pseudowollastonite	ps hexagonal	tabular prismatic	$\alpha CaOSiO_2$	αCS	α phase is more common than β phase	Parker, Ryder McCottery, Lord Ryder, Guttman
	Wollastonite	monoclinic	lath-shaped crystals	$\beta CaOSiO_2$	βCS	more common in low lime content. (c)	
Dicalcium silicate (calcium ortho-silicate)	Bredigite	...	...	$\alpha 2CaOSiO_2$	$\alpha' C_2S$	active and hydrate in slag of high lime. not acceptable for aggregate (c)	McCottery, Lord Guttman, Parker
	Larnite	orthorhombic	rounded grain	$\beta 2CaOSiO_2$	βC_2S		
	Dicalcium silicate	...	...	$\gamma 2CaOSiO_2$	γC_2S	inert (b)	
Forsterite		...	...	$2MgOSiO_2$	M_2S	...	...
Merwinite		monoclinic	grains	$3CaOMgO2SiO_2$	C_3MS_2	slag rich in magnesia	...
Rankinite		...	...	$3CaO2SiO_2$	C_3S_2	...	...
Monticellite		...	...	$CaOMgOSiO_2$	CMS	slag rich in magnesia	...
Diopside		...	...	$CaOMgO2SiO_2$	CMS_2	...	...
Spinel		...	...	$MgA\ell_2O_3$	MA	...	...
Anorthite		...	...	$CaOA\ell 2SiO_2$	CAS_2	occurs in low lime, high calcium slag (a)(c)	...
Calcium aluminate		...	...	$CaOA\ell_2O_3$	...	...	...
Calcium sulphide	Oldhamite	isometric	small sphere	CaS	...	...	Guttman, Parker Ryder, Brown
Olivine series		orthorhombic	equant	$2(MgOFeO)SiO_2$	...	...	Lord, Guttman
Alkalis		...	...	...	...	...	...
Iron		...	...	...	...	...	...
Manganese oxides		...	...	...	...	...	...

Columns (1)(2) from [44]; Columns (3)(4) from [43]
(a) from [44]
(b) from [43]
(c) from [38]

TABLE 2-6
SOME POSSIBLE ASSEMBLAGES OF MINERALS FROM THE QUATERNARY SYSTEM OF COMPOUNDS CaO, SiO_2, Al_2O_3 AND MgO IN BLAST FURNACE SLAG [43]

No. of Slags Out of 21 Examined	C_2AS-C_2MS_2 solid solution	C_2MS_2	C_2S	CS	C_3S_2	C_3MS_2	MA	CMS_2	CMS	CAS_2	M_2S	MgO
5	x		x		x					x		
5	x			x								
4	x			x	x							
3	x					x	x					
2	x						x			x		
1		x					x			x	x	
1		x				x	x		x			
Other Possible Assemblages Not Observed in the 21 Slags	x		x			x						
		x		x				x		x		
		x						x		x	x	
		x					x		x		x	
			x			x	x					x
						x	x		x			x

Some of the minor constituents are difficult to determine using microscope techniques because of the small amount and incomplete crystallization when the glassy phase is also present.

Physical Properties

While the physical characteristics of air-cooled blast furnace slag are somewhat variable from furnace to furnace and with time, they will tend to fall into a narrow range as indicated in Table 2-7. On the other hand, expanded and granulated blast furnace slags have a much wider range in physical characteristics since there are various processes and desired properties involved.

Utilization of Blast Furnace Slag

Blast furnace slag has been used in a wide range of applications. It is widely accepted throughout the world as a satisfactory aggregate with good performance in highway and building construction. With extra processing some blast furnace slag is also used in applications such as cement and mineral wool manufacture. A summary of blast furnace slag utilization and engineering advantages is given in Table 2-8. Possible engineering problems are shown in Table 2-9. (Care must be taken to distinguish between blast furnace and steel slag in Table 2-9.) Detailed data on blast furnace slag usage in the U.K. and U.S. are shown in Table 2-10 and 2-11, respectively. In 1967, the world consumption of blast furnace slag was at the order of one hundred million tons [44]. Data for 1966 [44-81] show about 30 million tons (representing 51.3 million dollars) used in the U.S., 15 million tons in Germany, 13 tons in France and 15 million tons in Japan.

TABLE 2-7

PHYSICAL PROPERTIES OF AIR-COOLED BLAST FURNACE SLAG AND STEEL SLAG

DESCRIPTION		BLAST FURNACE SLAGS			STEEL SLAGS	
		(a)	(b)	(c)	(d)	(e)
Sieve analysis		% passing				
sieve size	1 1/2"	100			grading as required	
	1"	62				
	3/4"	43				100.00
	1/2"	24	...	...		99.9
	3/8"	14				95.1
	#4	0				64.3
Dry weight lb/cu ft	loose	70.5(64.8-74.0)	...	...	...	110-130
	compact	83.5(75-88.2)	76.6	72.90	70-85	...
Absorption (24 hr)	%	2.5(1.7-3.7)	2.71-4.65	1.5-5	1-5	0.2-2.0
Bulk specific gravity		2.5(2.15-2.41)	2.32	2.38-2.76	2.0-2.5	3.2-3.5
Apparent specific gravity		...	2.45	...	...	...
Los Angeles Abrasion (A Grading)		32.72(29-39)	41.0	...	...	...
Soundness $MgSO_4$		...	2.47-1.41	...	...	<5
5 cycles	% loss					
Polished stone value		...	...	50-63	...	53-74

(a) from [7]
(b) from [17] Table No. 1 - National Slag Co., Hamilton
(c) from [44] British Slag Federation
(d) from [79] National Slag Association (air-cooled slag)
(e) from [23]

TABLE 2-8

UTILIZATION OF BLAST FURNACE SLAG AND ITS ENGINEERING ADVANTAGES

UTILIZATION	GENERAL ENGINEERING ADVANTAGES
AIR-COOLED SLAG Aggregate - structural concrete aggregate - concrete pavement aggregate - asphalt mix aggregate - base course for pavement Rail ballast Filter media Backfill - structure backfill - pipe backfill Glass making Land reclamation Slurry seal Slag surface treatment Slag roofing Mineral wool Septic tank absorption beds Ceramic ware [38] Oyster propagation [38]	angular particle controlled gradation as required roughness of surface texture hydrophobic nature lighter unit weight (less tonnage) high skid resistance hardness high polished stone value coefficient of friction fire resistance (from molten state) light colour (visibility) soundness less frost susceptibility
EXPANDED SLAG Lightweight structural concrete Structural concrete Concrete masonry unit	lightweight soundness nailability sound transmission thermal insulation property shrinkage
GRANULATED SLAG Base material for pavement Fill material Manufacture of cement Pipe backfill Concrete floor fill Concrete masonry unit Landscaping Agriculture	lightweight glassy material cementing property lime content

TABLE 2-9

UTILIZATION AND POSSIBLE PROBLEMS IN BLAST FURNACE SLAG AND STEEL SLAG

A. GENERAL UTILIZATION OF BLAST FURNACE SLAG AND STEEL SLAG (✓ USED, x NOT USED, ? NOT KNOWN)

UTILIZATION	BLAST FURNACE SLAG	STEEL SLAG
Concrete [9]	✓	x
Concrete Blocks [11,31]	✓	x
Aerated Concrete [9]	✓	?
Lightweight Aggregate [9,11,31,82]	✓	x
Bricks [9,11]	✓	x
Soil Stabilization [2,9]	✓	?
Cement Making [9,11,32]	✓	x
Grouting [9,84,87]	✓	✓
Ceramics [9]	✓	✓
Landfill [9,11,85]	✓	✓
Cultivation [9]	✓	✓
Road Base [11,88]	✓	✓
Asphalt Mix Filler [11]	✓	?
Sewage and Water Treatment [11]	✓	?
Mineral Wool [38]	✓	x

B. PROBLEMS IN UTILIZATION OF BLAST FURNACE SLAG AND STEEL SLAG

PROBLEMS	BLAST FURNACE SLAG	STEEL SLAG
Expansion [21,23]		✓
Corrosion in Steel Pipe [6]		✓
Corrosion in Reinforced Steel in Concrete [25]		✓
Alkali Reactivity [7]	✓	
Durability of Concrete with Slag [76]		✓
Sulphur Problem with Slag [33,76]	✓	✓

TABLE 2-10

SLAG USED IN THE U.K. IN 1967 [44]

DESCRIPTION	TONNAGE
Air-cooled Slag (a)	11,199,000 Tons
Road Stone	
chippings and coated and uncoated macadam and asphalt	9,308,000
rail ballast	758,000
filter media	192,000
concrete aggregate	148,000
unrecorded uses	793,000
Expanded Slag	207,000
Granulated Slag	83,000
Domestic Uses	183,000
TOTAL	11,672,000

(a) Tonnage of air-cooled slag includes about 470,000 tons of steel slag.

TABLE 2-11

BLAST FURNACE AND STEEL SLAG USAGE IN THE UNITED STATES DURING 1971 [102]

USE	MILLION TONS
AIR-COOLED BLAST FURNACE SLAG	
Aggregate in	
portland cement concrete construction	
structures	1.986
pavements	0.413
bituminous construction	4.091
highway and airport construction	8.285
manufacture of concrete block	0.469
Railroad ballast	3.174
Mineral wool	0.411
Roofing slag	
cover material	0.328
granules	0.063
Sewage trickling filter medium	0.036
Agricultural slag, liming	0.008
Other uses	2.180
TOTAL	21.444
VALUE	$42,352,000
GRANULATED AND EXPANDED BLAST FURNACE SLAG	
Highway construction and fill	0.997
Agricultural slag, liming	0.074
Manufacture of cement	0.457
Lightweight concrete	0.026
Aggregate for concrete block manufacture	1.447
Other uses	0.367
TOTAL	3.368
VALUE	$7,332,000
STEEL SLAG	
Railroad ballast	0.855
Highway bases or shoulders	2.635
Paved area base	1.115
Miscellaneous base or fill	2.053
Bituminous mixes	0.529
Agricultural	1.202
TOTAL	8.488
VALUE	$9,719,000

2-2-1-2 Steel Slag

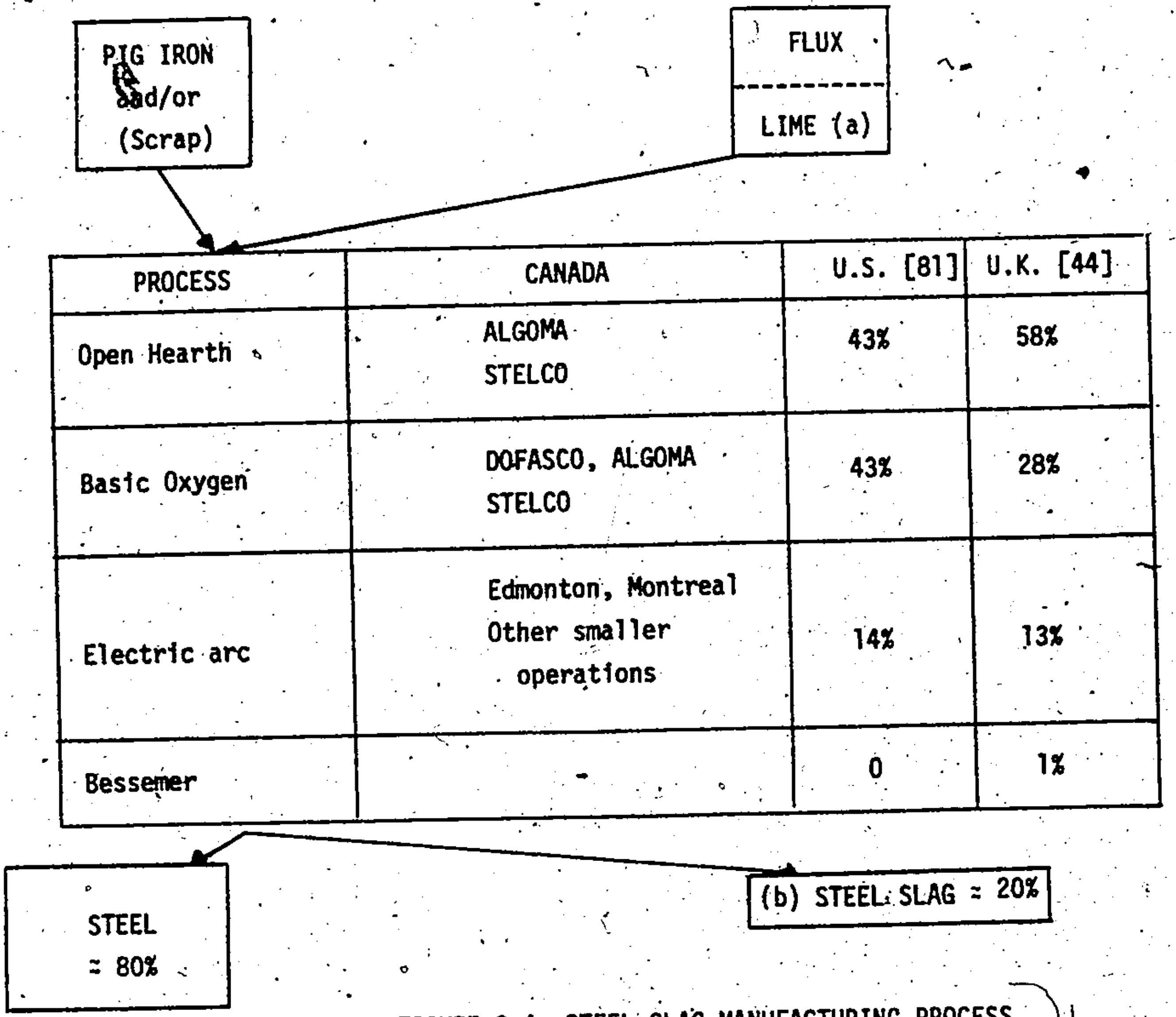
Manufacture of Steel Slag

While steel slag is a sister by-product of blast furnace slag as mentioned in the general classification of slags, it has some very different properties that limit its usage as compared to blast furnace slag. The different steel making processes used to convert pig iron (and/or steel scrap) to steel involve the removal of excess quantities of carbon, manganese, phosphorus and sulphur, and adding flux to generate different steel slags. These tend to be batch processes, with a consequently higher variability in the slags produced than is the case with blast furnace slags. Steel slags have received less attention and utilization than blast furnace slags in the past without any well founded reasons once the basic differences in properties and types of utilization are recognized. The typical processes used in steel making are the oxygen convertor (basic oxygen or LD process), open hearth furnace, electric arc and Bessemer Convertor. Figure 2-4 shows a brief process schematic for steel slag production during steel making.

Nowadays, steel making processes generally use lime as a flux instead of using limestone, resulting in a high free calcium content in the steel slags produced. The lime factor is approximately 25 and 125 lbs per ton of steel ingot produced in the open hearth and basic oxygen processes, respectively. Steel slags can be classified into two general groups [31] :

a) Phosphate rich slags (often used for fertilizer) which are no longer produced; and,

b) High calcium slags which are low in phosphates.



PROCESS	CANADA	U.S. [81]	U.K. [44]
Open Hearth	ALGOMA STELCO	43%	58%
Basic Oxygen	DOFASCO, ALGOMA STELCO	43%	28%
Electric arc	Edmonton, Montreal Other smaller operations	14%	13%
Bessemer	-	0	1%

FIGURE 2-4 STEEL SLAG MANUFACTURING PROCESS

(a) Lime factor 125 lb/ton of steel

(b) 400 lb/ton of Hot metal ≈ 50% goes to blast furnace for lime and FeO, Fe_2O_3
400-500 lb/ton of steel from [23]
444 lb/ton of steel from [81]

Only the high calcium slags are considered here.

Chemical Composition of Steel Slags

There is no basic difference in chemical constituents between steel and blast furnace slags, (see Table 2-4 for a comparison), but in chemical proportions, physical properties and usage, several important differences are apparent [23]. Steel slags have high iron contents (20 to 26%) which give a high specific gravity of 3.2 to 3.5 compared to 2.3 to 2.7 for air-cooled blast furnace slags. A high free lime content is another difference from blast furnace slag that is generally low in free lime. The mineralogical composition is basically different from that of blast furnace slag. Steel slags include tricalcium silicate ($3CaO\ SiO_2$), calcium orthosilicate ($\beta\ 2CaO\ SiO_2$), calcium oxide - ferrous oxide solid solutions ($2CaO\ Fe_2O_3/CaO\ Fe_2O_3$), and free lime (CaO) [23-31].

The presence of the metastable compound dicalcium silicate ($\beta\ 2CaO\ SiO_2$), which has a tendency to transfer to the γ form ($\gamma\ 2CaO\ SiO_2$) accompanied by a 10% volume increase, causes a "falling" effect and tricalcium silicate is potentially reactive [31]. This problem is usually obviated during handling, crushing and steel recovery. After crushing and steel recovery, steel slag may suffer long term instability from the hydration of particles of dolomite or magnesite that may become entrapped in the slag from the lining of the furnace, and free lime [44]. This problem is avoided in practice by aging the crushed slag for a period of up to a year or so before use [31]. Even so, there still may exist a risk of expansion from trapped lime still present after conditioning [21]. This can be checked for by a number of tests to determine the expansion potential of steel slag. This detrimental property forms the main objection to using steel slag as aggregate in confined applications or in the highly alkaline environment of portland cement concrete. Also, the high specific gravity (unit weight ≈ 120 lb/cu ft average) raises transportation costs significantly.

The main advantages of steel slag are its high stability and skid resistance when incorporated into bituminous pavements [23,44]. Current research is focused on these two favourable aspects of steel slag in asphalt mixes to develop user specifications. Also, much steel slag that has been properly aged or treated with spent pickle liquor is used as an aggregate in bases and ballast.

Since steel slag is high in iron, lime and manganese units, it is usually returned in varying percentages to the blast furnace as part of the burden. As this return increases, it is doubtful that much steel slag will be available as aggregate except from non-integrated electric arc or speciality steel operations. However, certain portions will always be available and this material should be used to best advantage.

Utilization of Steel Slag

The utilization of steel slag in the U.S. in 1971 was 8.5 million tons (Table 2-12). The projected increase in steel slag usage is shown in Table 2-12, but must be viewed as optimistic in light of efforts to return a higher percentage as blast furnace burden. About one-half million tons of steel slag was used in the U.K. in 1967 [44]. In the U.S., the use of steel slag asphalt mixes in the Detroit area was developed in 1962 as a program for low cost paving of side streets with an open hearth steel slag. The Edw. Levy Company in Detroit adopted a watering process for pop-out trouble in bituminous surfacing

TABLE 2-12

RATE OF GROWTH OF BLAST FURNACE AND STEEL SLAG USAGE IN U.S. [102]

SLAG	YEAR	MILLION TONS
Blast Furnace Slag Processed	1969	29.744
	1970	26.147
	1971	24.812
	1972	25.000*
	1973	25.500*
Steel Slag (sold or used by processors)	1969	7.299
	1970	7.539
	1971	8.488
	1972	9.300*
	1973	10.300*

* Projected

(approximately 250,000 tons per year), and treated the steel slag with spent pickle liquor for base construction in 1968, thus eliminating the heaving often experienced with improperly aged steel slag base. The use of steel slag asphalt mixes and precoated chippings (250,000 to 350,000 tons per year) by Steelphalt Limited in the English Midlands is detailed in a research report [23] of the Highway Materials Laboratory. In the U.K., steel slag is generally accepted as an excellent material for bituminous surfacings and chippings.

2-2-1-3 Fly Ash

Fly ash is a by-product of many industries since it results from the combustion of powdered coal. It has been more correctly termed Pulverized Fuel Ash (PFA) in Britain and this terminology is becoming more common. Fly ash is a member of the pozzolan family that also includes volcanic ash, obsidian, opaline, cherts, shales and diatomaceous earths. The terms pozzolan and fly ash are often used synonymously without recognizing that there are many other pozzolanic materials.

Pozzolans are defined by ASTM C593-69 as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in a finely divided form and in the presence of moisture, chemically react with calcium hydro oxide at ordinary temperatures to form compounds possessing cementitious properties". This definition implies the main chemical composition and nature of the pozzolanic reaction between pozzolan and lime.

Many investigators [2, 9, 31, 46, 56, 61, 63, 82] have studied the composition, properties, size, size distribution, manufacturing processes and pozzolanic reaction of fly ash. It is surprising from the volume of this research that so little actual use is made of fly ash in North America.

Sources of Fly Ash

The chief source of fly ash is electric power plants which use powdered coal as fuel for their steam boilers. A brief schematic flow chart of fly ash production in a thermal plant is shown in Figure 2-5.

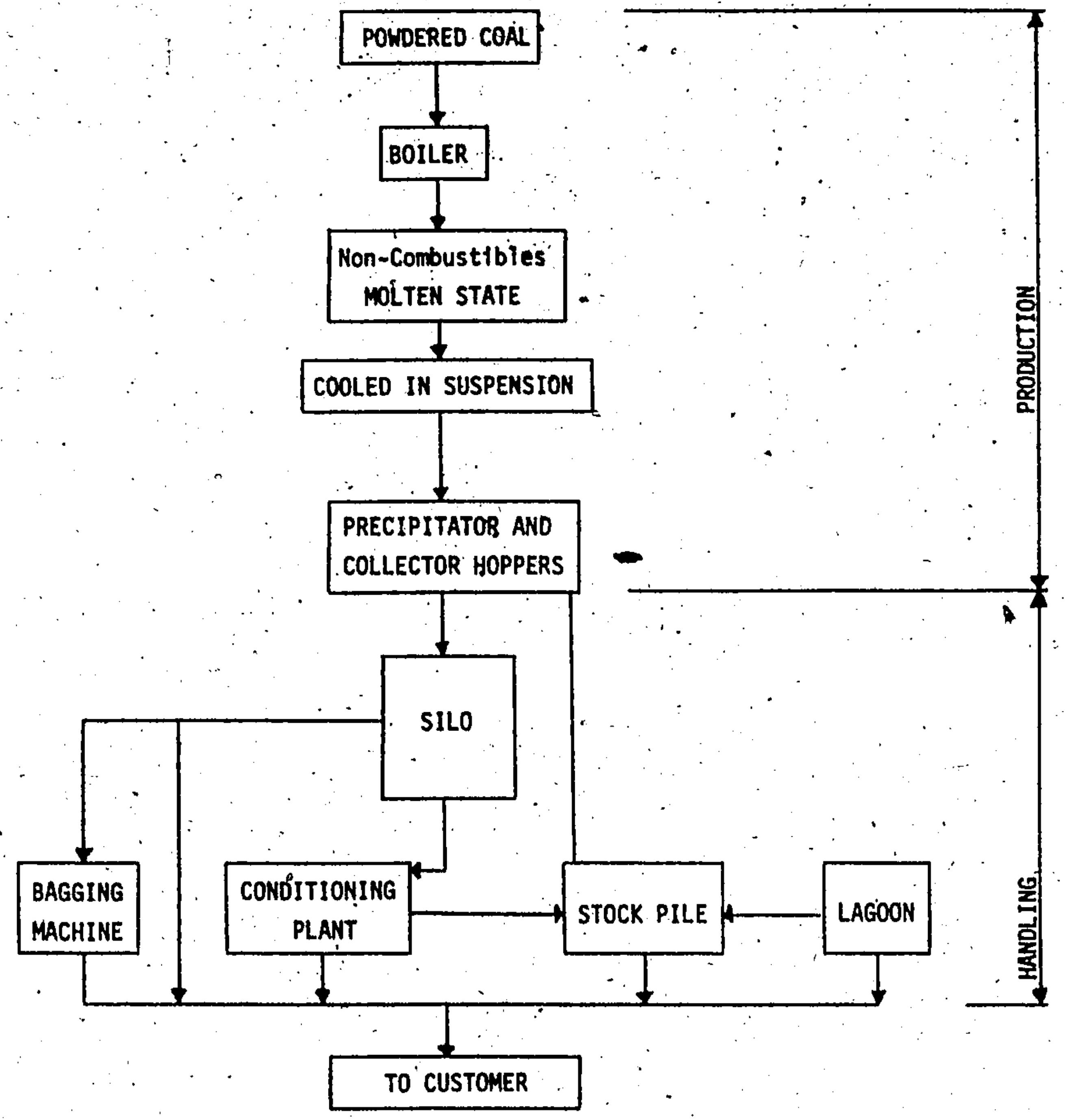


FIGURE 2-5 PRODUCTION AND HANDLING OF FLY ASH

Powdered coal is burned and the various non-combusted impurities remaining that form fly ash are cooled from the molten state in suspension. This fly ash is collected from the flue gases by mechanical precipitators which generally collect a coarser product, and electro-static precipitators which collect a finer one. Fly ash, which is about 65% of the total residue, is accompanied by about 25% bottom ash and 10% boiler slag. This boiler slag generally finds an excellent market because it is similar to blast furnace slag. Fly ash often receives further processing - beneficiation [9, 11, 31, 83] - partially eliminates carbon, iron, and sulphur and separates the particles by fineness. Processes to pelletize, sinter and screen fly ash to produce lightweight aggregate are also used. A beneficiating plant is operated (with some technical problems) by Ontario Hydro at its Lakeview thermal plant.

Chemical Composition

Although the general nature and properties of various fly ashes are somewhat similar, fly ashes differ not only as a function of the type and efficiency of the precipitation equipment, but also as a function of the composition and fineness of the coal, and the efficiency and type of combustion procedure. Generally, the fly ash produced during load operation is superior to that produced during peaking.

Fly ash consists of about 75% silica and alumina, and small amounts of alkalis, carbon, calcium oxide, magnesium, sulphur and iron oxide. A typical range for the chemical composition is given in Table 2-13. Ferric oxide, aluminium oxide, and sulphur dioxide tend to concentrate in the finer particles, whereas the carbon in the coarser ones [2].

TABLE 2-13

COMPOSITION OF FLY ASH [9]

MAIN CONSTITUENTS		PERCENT
Silica	SiO_2	45-51
Alumina	Al_2O_3	24-32
Iron Oxide	Fe_2O_3	7-11
Calcium Oxide	CaO	1.1-5.4
Magnesia	MgO	1.5-4.4
Potassium Oxide	K_2O	2.8-4.5
Sodium Oxide	Na_2O	0.9-1.7

Physical Properties

Fly ash generally goes from a cream to dark grey colour as the carbon, iron and moisture content increases. Fly ashes are primarily solid, or hollow, amorphous, glassy particles with some crystalline zones, spherical in shape with a Blaine fineness of 2000 to 6000 sq cm/gr. Their specific gravity ranges from 2.0 to 2.8 and there is a significant difference between individual particles. A comparison of the particle size with that of soils is given in Figure 2-6. As indicated, the particle size of fly ash ranges within that of a silty soil. This may be important since this size of soil is often frost susceptible.

An investigation of two types of fly ash from a size viewpoint; one a coarse fly ash collected by mechanical precipitators, the other a fine fly ash collected by electrostatic precipitators is reported in Reference 46. The percentage of amorphous glass clearly appears to increase with decreasing particle size for both types. The compositions of both fly ashes are shown in Table 2-14. The samples were wet-sieved and examined as oil immersion mounts with a petrographic microscope.

The finer fly ash contained 87% glass in the -#500 sieve size portion compared with only 63% in this portion for the coarser fly ash. The reason for this difference is the method of collection. In collecting the coarser ash, large amounts of the finer material in which the glass is concentrated escape up the stacks due to the low efficiency of mechanical devices in collecting finer ash. The glass consisted of colourless to light green and amber spheres. Carbon particles were about three times more abundant in the coarser fly ash than in the finer ash.

The chemical analysis relating to particle size groups from each

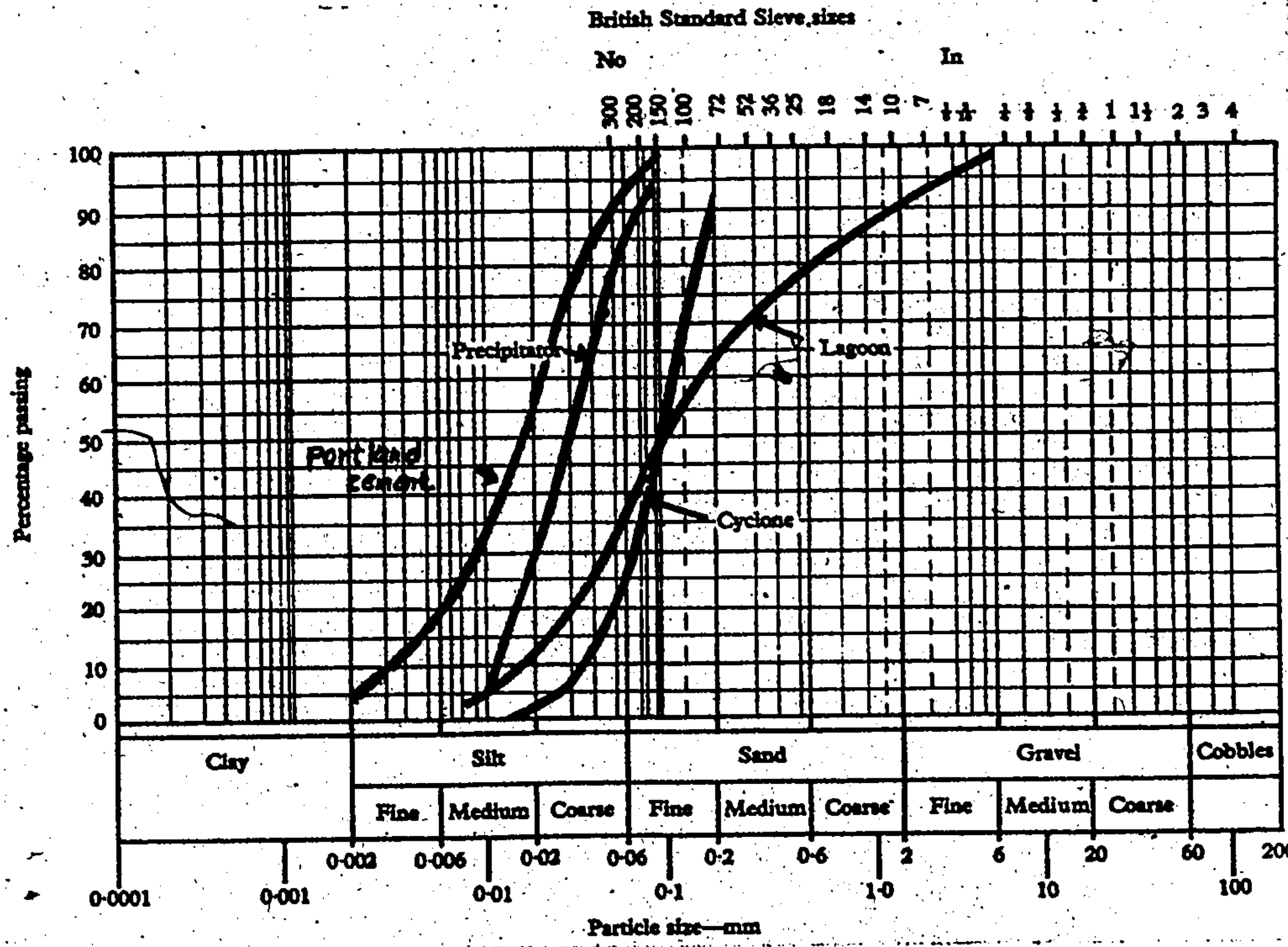


FIGURE 2-6 PARTICLE SIZE COMPARISON BETWEEN PORTLAND CEMENT, FLY ASH AND SOIL [9]

TABLE 2-14

PARTICLE SIZE OF FLY ASH AND CONSTITUENTS [46]

CONSTITUENT	AD-3 (FINER FLY ASH)						AD-94 (COARSER FLY ASH)					
	PERCENT RETAINED (a)					COMPOSITION OF TOTAL SAMPLE (b)	PERCENT RETAINED (a)					COMPOSITION OF TOTAL SAMPLE (b)
	#200	#325	#400	#500	-#500	%	#200	#325	#400	#500	-#500	%
Glass	32	49	52	56	87	79	33	55	61	58	63	58
Magnetite-hematite	2	14	13	14	5	6	8	5	20	26	16	16
Carbon	33	8	9	5	1	4	47	29	7	8	5	13
Anisotropic material	27	22	18	15	3	6	3	3	3	3	5	4
Aggregates	6	7	8	10	4	5	7	8	9	5	11	9
Total	100	100	100	100	100	100	100	100	100	100	100	100

(a) Percentage is based on count of more than 300 particles in each sieve fraction.

(b) Percentage is based on gradation of as-received sample and on the distribution of constituents of wet sieved fractions.

sample indicated that the coarser the fly ash, the more iron content and the less silica and alumina content the fly ash has. Table 2-15 shows more details of these results.

The relationship between the silica, alumina and glass content and particle size distribution influences the pozzolonic reaction of the fly ash with lime and moisture.

Utilization of Fly Ash

The total power plant ash collected in the U.S. in 1971 amounted to 42.8 million tons [61, 83], including 27.8 million tons of fly ash, 10.0 million tons of bottom ash and 5.0 million tons of boiler slags. Only about 11.7% of the fly ash, or 3.25 million tons, was utilized in various useful purposes. Data for Canada is generally not available and the percent utilization is probably even lower. Obviously, the production of fly ash is rapidly increasing as thermal power generation takes up a larger element of power capacity. At present, Ontario is producing close to 600,000 tons per year. A corresponding increase in outlets for what is still largely a waste product must still be developed. At present, the greatest progress in fly ash utilization is in the U.K. and Europe. The National Ash Association in the U.S. and the Central Electricity Generating Board in the U.K. are very active in promoting the use of fly ash. Activity in Canada is largely focused in Alberta and Ontario, with no national organization. The utilization and engineering advantages of fly ash are summarized in Table 2-16.

TABLE 2-15

PARTICLE SIZE AND CHEMICAL COMPOSITION [46]

TEST RESULT	COARSER FLY ASH (%)				AD-3 FINER FLY ASH (%)			
	AS RECEIVED	AD-94 PROCESSED			AS RECEIVED	PROCESSED		
		FINE	MEDIUM	COARSE		FINE	MEDIUM	COARSE
SiO_2	41.57	44.65	37.57	33.08	44.29	46.38	36.40	26.72
$A\ell_2O_3$	18.53	18.19	14.19	13.05	17.94	18.36	15.48	9.53
Fe_2O_3	24.33	19.87	38.23	43.46	19.64	16.46	37.28	53.35
CaO	4.83	5.07	4.00	5.56	6.67	6.61	5.08	4.92
MgO	0.96	0.78	0.86	0.71	1.03	0.91	0.72	0.59
Sulphide Sulphur	0.05	0.00	0.01	0.07	0.00	0.00	0.005	0.02
SO_3	0.64	0.70	0.42	0.76	2.40	2.60	0.87	0.74
Ignition loss	4.34	5.61	0.80	0.20	2.64	2.87	2.44	1.49
Na_2O	0.23	0.24	0.17	0.20	0.94	1.20	0.51	0.36
K_2O	1.96	2.01	1.54	1.23	1.90	2.03	1.20	0.86
Total alkalis as Na_2O	1.52	1.62	1.18	1.01	2.19	2.54	1.30	0.93
Total carbon	3.68	4.75	0.72	0.36	1.53	1.[illegible]0	2.04	1.19
Moisture loss	0.28	0.26	0.08	0.11	0.43	0.65	0.24	0.18
Insoluble residue	84.40	82.92	89.26	73.82	75.68	75.72	87.13	83.99

TABLE 2-16

UTILIZATION AND ENGINEERING ADVANTAGES OF FLY ASH

UTILIZATION	GENERAL ENGINEERING ADVANTAGES
Land fill	inert, cultivation easy
Partial replacement of cement in concrete product structural concrete dams or other mass concrete aerated concrete	improved workability, reduced segregation and bleeding, high strength, low permeability, reduced shrinkage, more finishable, low volume change, low heat in hydration, low alkali-aggregate reaction, better sulphate and acid resistance
Lightweight aggregate	sintered lightweight pellets
Filler in asphalt mix	-#200, hydrophobic (for stripping)
Filler in bituminous products	void filling and stability capacity
Soil improving agent	lightweight
Soil stabilization	cementing properties, no frost susceptibility
Cement manufacture	pozzolanic activity
Filler in rubber	chemical properties, inert
Filler for paint and putty	inert
Repairing top rot in power poles	spherical particles, smooth mixture
As insulation	thermal insulating properties
Raw material for glass	siliceous
Raw material for bricks	aggregates
Miscellaneous types of building blocks	same as concrete
Cementing materials for miscellaneous aggregates	pozzolanic activity
Filter layer under pavement	workability, fillability, non-frost susceptibility
Foundry work	for sand
Sand blasting	replace sand
Concrete pipe	workability
Precast concrete products	high strength
Prestressed concrete units	finishability
Grouting	spherical particles, inert, smooth mixture
Lightweight concrete	sintered aggregate
Oil well sealing	...
Ceramics	same as glass
Cultivation of land (soil conditioner)	adaptability of plant
Road base	pozzolanic activity
Sewage and water treatment	...
Pumping concrete	workability
Mine fire control	spherical, dense, pumpability
Anti-skid winter roads	...
Fertilizer filler	...
Vanadium recovery	...
Dust control	...

2-2-1-4 Steel Pickle Liquors [23, 54]

Major steel products such as sheets, strip, wire and galvanized pipe are suitably treated for the purpose of removing oxide scale by immersion in acid baths. This process is called "pickling", and the various acids used are termed pickle liquors. With use, the pickle liquors lose their effectiveness and must be discarded, or regenerated if possible. These acids include the following, either individually or in combinations [54].

Sulphuric acid	H_2SO_4
Hydrochloric acid	$HC\ell$
Nitric acid	HNO_3
Hydrofluoric acid	HF
Phosphoric acid	H_3PO_3

Among these, sulphuric acid is presently used for 90% of the steel tonnage pickled, but this figure will most probably be reduced as $HC\ell$ regeneration becomes more common. The average output of spent pickle liquor per ton of pickled products is approximately 50 gallons [54].

The two processes generally used for pickling are:

1. Acid bath process.

   An acid bath is used in which the products are suspended until pickling is complete. The spent H_2SO_4 liquor usually contains 0.5% to 2.0% free acid and 15% to 20% ferrous sulphate (as $FeSO_4$).

2. Continuous pickling process.

   This process involves passing a steel strip from a coil through a scale breaker, an automatic welder or stitcher, a series of tanks containing pickling liquor, a rinsing device and then a drier. The spent H_2SO_4 liquor in this process contains 4% to 7% free acid and 14% to 16% ferrous sulphate. While the use of H_2SO_4 in these processes has been indicated, the other pickle liquors can also be used.

Where it is possible to recover the spent pickle liquor before disposal, it can be regenerated through rather sophisticated processes. Spent $HC\ell$ pickle liquor regeneration systems have been developed and are in operation at many steel mills, including STELCO and DOFASCO in Hamilton. Progress with spent H_2SO_4 regeneration has been slower. A recently developed H_2SO_4 pickle liquor regeneration process is the Blaw-Knox-Ruthner method [54]. It is of enough interest and application to briefly describe. This process starts with the concentration of waste pickle liquor before discharging it into a reactor, where the ferrous sulphate is turned into reusable H_2SO_4 and $FeC\ell_2$ by anhydrous hydrogen chloride gas. At the roaster, the recoverable iron is then separated from the $FeC\ell_2$ and converted into iron oxide, liberating $HC\ell$ which is recovered and recycled to the reactor. This process and the chemical reactions involved are shown in Figure 2-7 [54].

Spent pickle liquors that are not regenerated (and other waste acids) can be discarded in deep wells, fissures in cavernous limestone, abandoned mines, exhausted oil and gas sands, artificial lagoons, gravel dumps near large bodies of water, sewers flowing into rivers, lakes or tide water without treatment, often resulting in pollution problems. Some treatment should be imposed upon the acid waste to neutralize

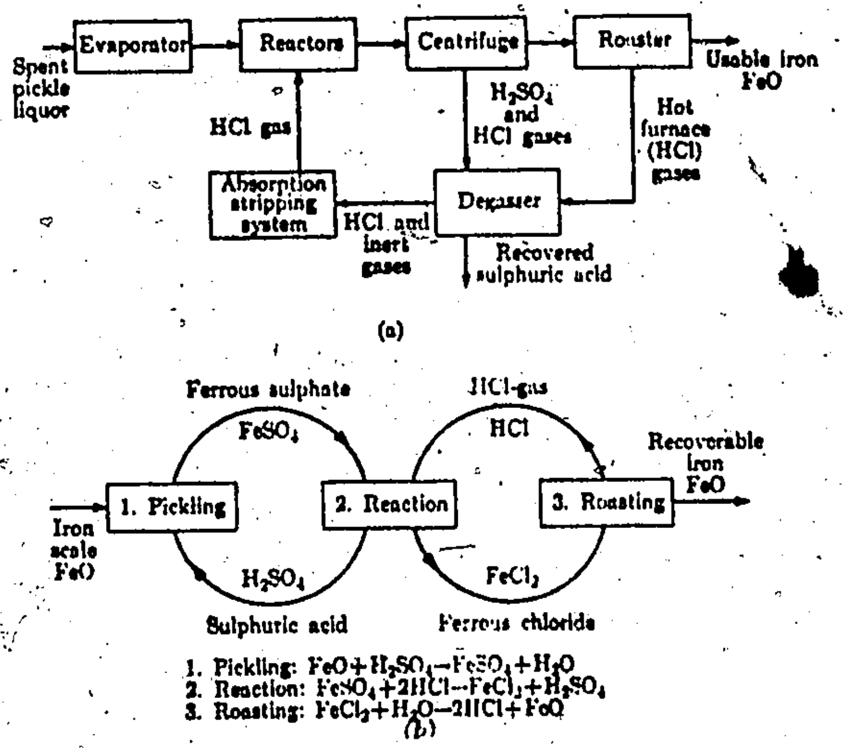


FIGURE 2-7 BLAW-KNOX-RUTHNER PROCESS FOR RECOVERY OF ACID FROM SPENT PICKLE LIQUOR

(a) PROCESS FLOW DIAGRAM.

(b) CHEMISTRY OF PROCESS [54].

the free acid with lime and to precipitate the iron and trace heavy metals (which can present a severe environmental problem). This problem is often solved through a standard municipal sewage treatment plant with an actual mutual benefit to both the municipality and producer, since ferrous sulphate or ferric chloride is an excellent coagulant for sewage and aids in phosphate removal [54]. This technique for sewage treatment is currently so popular that it has become more profitable to sell spent pickle liquors rather than to attempt regeneration. Research on this topic is being conducted at the Canadian Centre for Inland Waters [105]. Waste pickle liquors are being applied to fresh steel slag, which is highly alkaline and expansive, to accelerate any potential swelling before construction use. The Edw. Levy Company has found this to be a very suitable process in the Detroit area. This application has relieved the heaving of steel slag bases [23] and also provides an economic disposal method for spent acids. The question of heavy metal contamination does not appear to have been examined for such treatment.

2-2-2 Commercial Materials Associated with Waste Material Utilization

2-2-2-1 Lime

Lime is defined by ASTM C51-71 as "a general term which includes the various chemical and physical forms of quicklime, hydrated lime, and hydraulic lime used for any purpose". The types of lime along with their corresponding chemical compositions and physical properties are shown in Table 2-17.

The important properties of lime to point out are:

1. The hydration of quicklime generates heat.
2. The solubility of lime decreases with rising temperature.
3. Calcium ions are continually going into solution and recombining with the hydroxyl ions until the solution is saturated or a state of equilibrium is reached.

Seventeen million tons of lime were used in the U.S. in 1970. Lime is the second "greatest basic chemical", sulphuric acid being considered the first. It is used in a wide range of fields as shown in Table 2-18.

There are some forms of waste lime with varying compositions that may find use in, or as construction materials - kiln dust from portland cement manufacture and residues from the manufacture of acetylene are the most common. While the quantities available are small, research on these waste limes may generate a source of low grade lime suitable for pozzolanic reactions.

TABLE 2-17

COMMERCIAL LIME

TYPE OF LIME		QUICK LIME (UNSLAKED LIME)			HYDRATED LIME (SLAKED LIME)			HYDRAULIC LIME
		HIGH CALCIUM CaO	DOLOMITIC CaO+MgO	MAGNESIA CaO+MgO	HIGH CALCIUM $Ca(OH)_2$	MONO HYDRATED DOLOMITIC $Ca(OH)_2$+MgO	DIHYDRATED DOLOMITIC $Ca(OH)_2$+$Mg(OH)_2$	
Raw Materials for Lime	Limestone ($CaCO_3$)	x	...	...	x	...	...	...
	Dolomite or Dolomitic limestone	...	x	...	...	x	x	...
Hydration	Normal condition	...	...	...	x	x	...	...
	Under high pressure	...	...	...	...	...	x	...
Chemical Composition percent	CaO	92-98	55.5-57.5	...	$CaO+H_2O = Ca(OH)_2$ crystallization Chemical composition reflects the composition of quicklime from which it is derived.			...
	MgO	0.3-2.5	37.6-40.8	5.0-35.0				
	CO_2	0.4-1.5	0.4-1.5	...				
	SiO_2	0.2-1.5	0.1-1.5	...				
	Fe_2O_3	0.1-0.4	0.05-0.40	...				
	$A\ell_2O_3$	0.1-0.5	0.05-0.50	...				
	H_2O	0.1-0.9	0.10-0.90	...				
Physical Properties	Specific gravity	3.2-3.4	3.2-3.4	...	2.3-2.4	2.7-2.9	2.4-2.6	...
	Specific heat at 100°F (Btu/pound)	0.19	0.21	...	0.29	0.29	0.29	...
	Bulk density (pcf)	55-60	55-60	...	25-35	25-35	30-40	...
Size of Lime	8"-2"	Lump lime			Dry powder			...
	2"-1/4"	Crushed or pebble lime						
	#8-#80	Granular lime						
	100%-#8-40-60%-#100	Ground lime						
	100%-#20-85-90%-#100	Pulverized lime						
	one in size pellets	Pelletized lime						

TABLE 2-18

USAGE OF LIME

Soil Stabilization
Steel Manufacture
Pulp and Paper
Chemicals
Water Treatment
Sewage Treatment, Industrial Waste Treatment
Ceramic Products
Building Material
Protective Coating
Food and Food By-product
Others

2-2-2-2 Calcium Chloride, $CaC\ell_2$

Calcium chloride is a by-product of sodium carbonate (Na_2CO_3) and is extremely deliquescent. Calcium chloride is very soluble, even at low temperatures. The physical properties of pure anhydrous calcium chloride and its hydrates are shown in Table 2-19.

It has long been used as a dust control measure for unpaved roads and tennis courts. Anhydrous calcium chloride is often used for "air drying" ($CaC\ell_2.H_2O \rightleftarrows CaC\ell_2 + H_2O$). Calcium chloride is widely accepted as an additive for portland cement concrete to accelerate the rate of hydration of the cement. This faster rate of hydration, especially for concrete placed during low temperatures, produces the beneficial effects of reduction in time for set, early strength and protection of the fresh concrete [13, 89].

Soil-aggregates for pavement bases can often have their stability improved by the addition of calcium chloride which decreases the plasticity of fine soils [62, 64, 90].

TABLE 2-19

PHYSICAL PROPERTIES OF PURE ANHYDROUS CALCIUM CHLORIDE AND ITS HYDRATES [101]

PROPERTIES OF ANHYDROUS CALCIUM CHLORIDE

Molecular weight	110.99
Melting point	772°C (1424°F)
Boiling point	above 1600°C
Specific gravity	2.152 at 15/4°C 2.26 at 20/4°C
Specific heat at 61°C (141.8°F)	0.164 cal/g/°C 0.164 Btu/lb/°F
Latent heat of fusion at 772°C	54.2 cal/g 97.6 Btu/lb
Heat of formation at 18°C (64.4°F)	190.6 kg-cal/gfw 3090 Btu/lb
Heat of solution at 18°C (64.4°F) in 400 moles of water	17.99 kg-cal/gfw 292 Btu/lb
Coefficient of expansion	0.00062

PROPERTIES OF CALCIUM CHLORIDE MONOHYDRATE ($CaC\ell_2 \cdot H_2O$)

Composition	86.0% $CaC\ell_2$ 14.0% H_2O
Molecular weight	129.01
Melting point	260°C (500°F)
Heat of formation at 18°C (64.4°F)	265.23 kg-cal/gfw 3700 Btu/lb
Heat of solution at 18°C (64.4°F) in 300 moles of water	11.71 kg-cal/gfw 163 Btu/lb

PROPERTIES OF CALCIUM CHLORIDE DIHYDRATE ($CaC\ell_2 \cdot 2H_2O$)

Composition	75.5% $CaC\ell_2$ 24.5% H_2O
Molecular weight	147.03
Melting point	175.5°C (347.9°F)
Heat of formation at 18°C (64.4°F)	333.25 kg-cal/gfw 4080 But/lb
Heat of solution at 18°C (64.4°F) in 400 moles of water	10.04 kg-cal/gfw 123 Btu/lb

PROPERTIES OF CALCIUM CHLORIDE TETRAHYDRATE ($CaC\ell_2 \cdot 4H_2O$)

Composition	60.6% $CaC\ell_2$ 39.4% H_2O
Molecular weight	183.05
Melting point	45.3°C (113.5°F)
Heat of formation at 18°C (64.4°F)	480.17 kg-cal/gfw 4722 Btu/lb
Heat of solution at 18°C (64.4°F) in 400 moles of water	2.2 kg-cal/gfw 21.6 Btu/lb

PROPERTIES OF CALCIUM CHLORIDE HEXAHYDRATE ($CaC\ell_2 \cdot 6H_2O$)

Composition	50.7% $CaC\ell_2$ 49.3% H_2O
Molecular weight	219.09
Specific gravity	1.7182 at 4°/4°C 1.68 at 17°/17°C
Melting point	29.92°C (85.8°F)
Specific heat at 0°C (32°F)	0.320 cal/g/°C 0.320 Btu/lb/°F
Latent heat of fusion at 29.92°C (85.8°F)	40.7 cal/g 73.4 Btu/lb
Heat of formation at 18°C (64.4°F)	623.3 kg-cal/gfw 5120 Btu/lb
Heat of solution at 18°C (64.4°F) in 400 moles of water	-4.34 kg-cal/gfw -36 Btu/lb

2-2-2-3 Emulsified Asphalt [42, 53, 91, 92]

Emulsified asphalt forms a small portion of the bituminous material classification in Figure 2-8. The main process for emulsified asphalt production is shown in Figure 2-9.

Bitumen consists mainly of: asphaltenes (hydrocarbons) which form the body of asphalts; resins which give the adhesive and ductile properties that are lost by oxidation; and, oils which are the source of viscosity and flow properties. These constituents are shown in Figure 2-10. At present, two main types of bituminous material are used in road construction, namely, asphalt and tar. The main source of asphalt is the refining of petroleum. Tar products come mainly from coking operations. With recent shortages in petroleum products, the cost of both asphalt and tar has escalated since their fuel values are relatively high (from approximatley $35 per ton for penetration grade asphalt last year to over $75 per ton this year).

Emulsified asphalts are intimate mixtures of two immiscible liquids - asphalt and water - one of which (asphalt) is dispersed in the other (water) in the form of very tiny droplets along with the emulsifying agent. This emulsifying agent affects the chemical and physical properties of the particular emulsified asphalts. Emulsified asphalts are made by mechanically dispersing a liquid asphalt in water which has already been treated with an emulsifying agent as indicated previously in Figure 2-9. A colloid mill is used which breaks the asphalt into colloid-size particles by generating high shearing forces.

BITUMEN	SOURCES	STATES	FLUXING MATERIAL	USAGE	SPECIFICATION
Bituminous materials	Asphalt — Native asphalt	Solid — Lake asphalt Rock asphalt Other native asphalt (Gilsonite)			
	Asphalt — Petroleum asphalt (asphaltic-base crude oil)	Solid asphalt (semi-solid) — Asphalt cement		High class highway	ASTM D946 AASHO M20
		Solid asphalt (semi-solid) — Blown asphalt		Waterproofing Joint sealing Roofing	
		Liquid asphalt — Cut back asphalt — Rapid curing	Gasoline or Naptha	Lower class road (secondary) Maintenance Surface treatment	ASTM D2028, AASHO M81
		Cut back asphalt — Medium curing	Kerosene		ASTM D2027 AASHO M82
		Cut back asphalt — Slow curing	Slowly volatile oil		ASTM D2026 AASHO MT41
		Emulsified asphalt — Anionic — Rapid setting RS-1	Water and emulsifier	Tack coating (T.C.) Surface treatment (S.T.) Prime coat (P.C.)	ASTM D977 AASHO MT40
		RS-2		S.T., P.C.	
		Medium setting MS-1		T.C., P.C.	
		MS-2 MS-2h		P.C.	
		Slow setting SS-1 SS-1h		P.C. Slurry seal	
		Cationic — R.S. CRS-1		S.T., T.C., P.C.	ASTM D2397 AASHO M208
		CRS-2		S.T., P.C.	
		M.S. CMS-2 CMS-2h		P.C.	
		S.S. CSS-1 CSS-1h		P.C. Slurry seal	
		Road oil	Non volatile oil	Dust control	
	Tar — Cracking of petroleum (watergas tar)				
	Tar — Destructive (distillation of coal)	Coke oven tar Gas house tar			

FIGURE 2-8 CLASSIFICATION OF BITUMINOUS MATERIALS

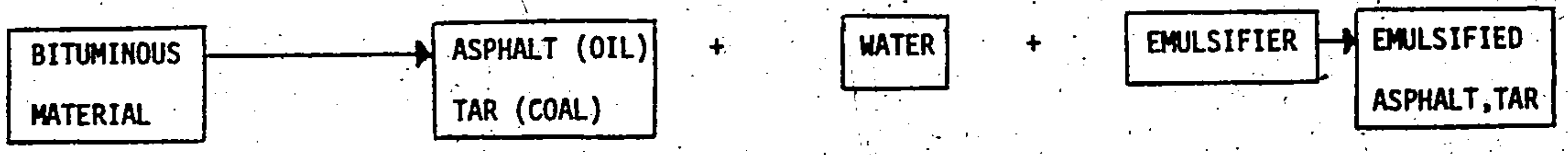


FIGURE 2-9 EMULSIFIED ASPHALT PRODUCTION

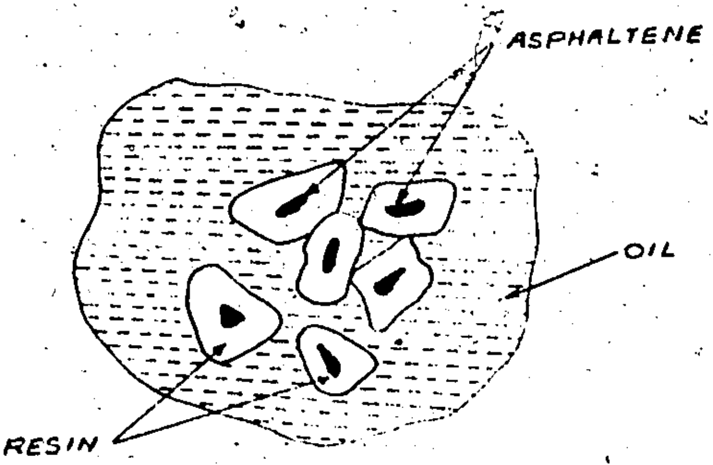
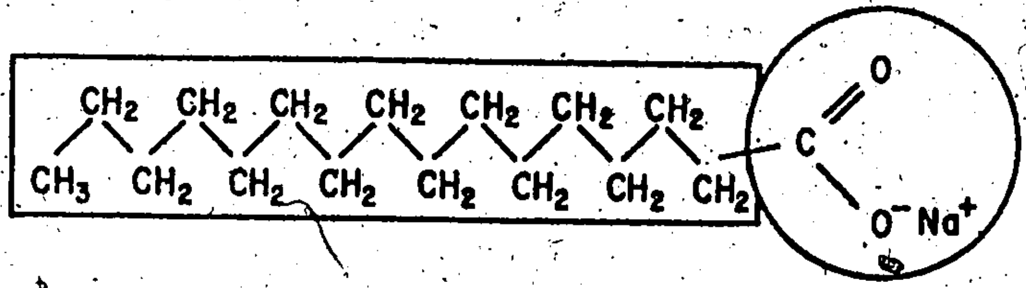


FIGURE 2-10 COMPOSITION OF ASPHALT

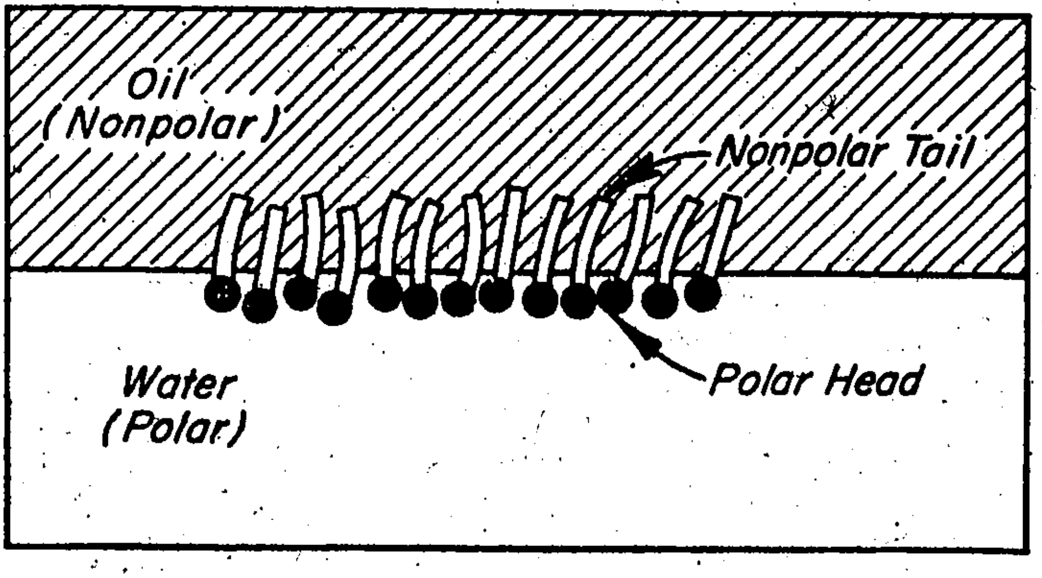
The asphalt particles in the emulsified asphalt are covered by the emulsifying agents which are combined polar and non-polar molecules termed surface active molecules. These particles are prevented from combining with other particles due to the repulsive force between like charged particles. A sketch of one such molecule of emulsifying agent, sodium palmitate is shown in Figure 2-11 (a).

The left side of the molecule is the non-polar portion and is soluble in oil, the right side is the polar part and water soluble. When the asphalt and water are mixed with this agent, an orientation of the surface-active molecules occurs at the interface between asphalt and water, as shown in Figure 2-11 (b). The active part of the surface-active molecule will ionize and dissociate in water. Anionic emulsified asphalts result from a negative charge at the surface of asphalt particles (anionic-sodium palmitate agent), whereas cationic results from a positive charge (cationic-lauryltrimethylammonium chloride agent).

There are many advantages in the use of emulsified asphalts over other liquid asphalts. The prime one is being able to get asphalt to bond to aggregates which carry a surface charge dependent on the mineralogic composition of the original rock. If the charge on the surface of the aggregate is negative (quartz, for example), a cationic emulsion which carries a positive charge will allow bonding to take place. The other advantages are that emulsified asphalt can be used with aggregate which is dry, damp, or wet and it eliminates many fire and toxicity hazards during construction. Both anionic and cationic emulsions are used depending on the properties desired. Cationic emulsions are a relatively



(a) Sodium palmitate



(b) Adsorption of emulsified asphalt molecules at an interface

FIGURE 2-11 SODIUM PALMITATE EMULSIFIED ASPHALT [53] new development designed for the large class of acidic aggregates such as quartzite. Subtypes, usage recommendations, and specification designations for emulsified asphalts are shown in Figure 2-8.

Current research with emulsified asphalts appears to be focused on base stabilization or combined base stabilization with other chemical stabilizing agents [23]. The aim is to decrease the cost of cementing agents in highway construction.

2-3 CEMENTING PROPERTIES OF COMBINED AND/OR PROCESSED MATERIALS

2-3-1 Portland Cement and Other Related Cementing Materials

2-3-1-1 Portland Cement

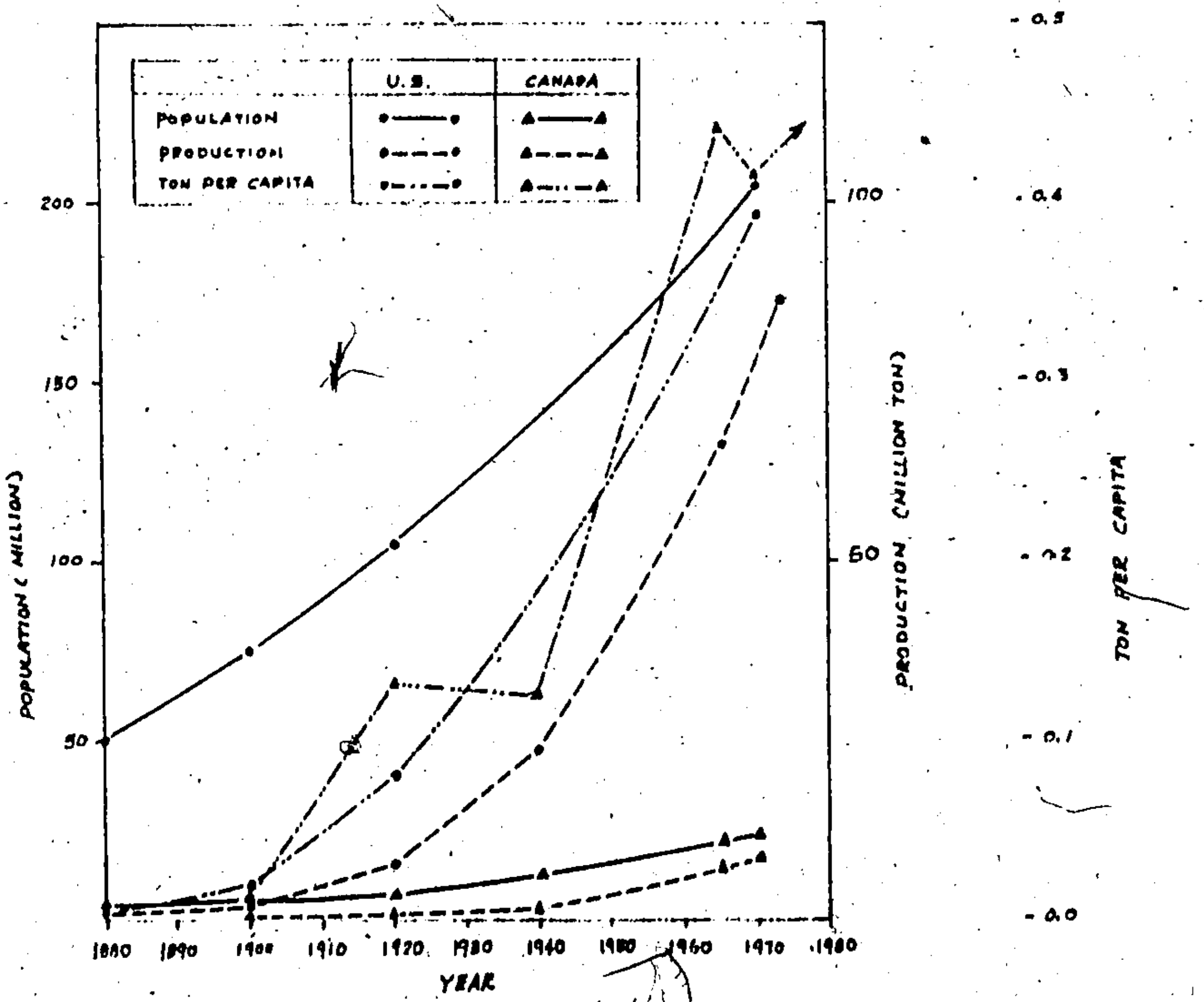
Portland cement, the name of which originates from its resemblance to a natural building stone quarried at Portland, England, is defined in ASTM C150-74 as "hydraulic calcium silicates". It was patented by Joseph Aspdin, an Englishman in 1824, and first made commercially in the U.S. in 1870. Portland cement was first used in reinforced concrete in 1868. Since its development, the growth of portland cement production has been rapid as shown in Table 2-20. The annual production reached 81.4 million tons in the U.S. in 1972 [95] and 9 million tons in Canada in 1971 [75]. The trends from the past capacity and consumption, and future projections in U.S. cement manufacturing as shown in Figure 2-12 indicate that: in the 1960's, capacity was much higher than consumption for domestic use; at the beginning of the 1970's the capacity and consumption were nearly balanced; and, thereafter a great shortage is indicated. For the first time, an actual shortage was reported in the U.S. in 1969. Cement and clinker import data (mainly from Canada) indicate that this shortage amounted to 2.60 million tons in 1970, 3.09 million tons in 1971, and 4.91 million tons in 1972 [95].

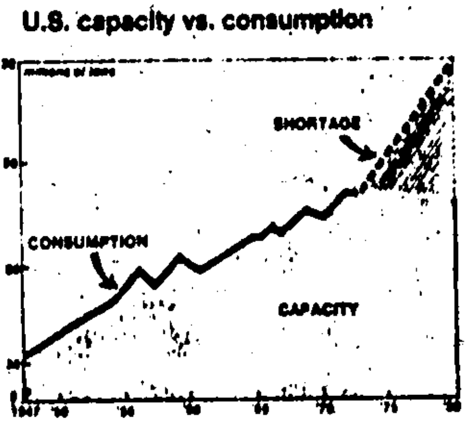
During the 1960's, the return on investment in the cement industry was down to about 6%, but has risen back to about 10% during the past three years in the U.S [34]. These figures make 1974 the turning point for cement production with eleven major plant expansions and construction of two new plants underway with a combined production increase of 4.7

TABLE 2-20

PRODUCTION OF PORTLAND CEMENT IN U.S. AND CANADA

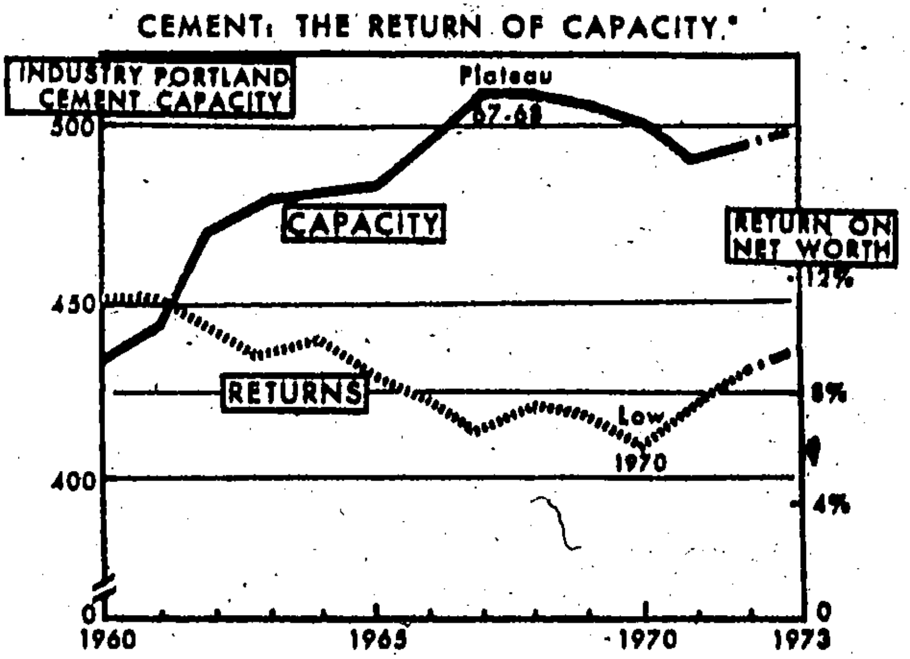
	PRODUCTION (TON)		POPULATION		CEMENT PRODUCTION PER CAPITA	
	U.S.	CANADA	U.S.	CANADA	U.S.	CANADA
1880	8,000	...	50,000,000	4,300,000	0.00016	...
1900	1,600,000	78,000	76,000,000	5,370,000	0.021	0.015
1920	8,800,000	1,220,000	105,700,000	8,790,000	0.083	0.138
1940	24,600,000	1,416,000	...	11,500,000	...	0.123
1960	67,146,000	8,830,000	...	20,000,000	...	0.446
1970	...	7,780,000	203,000,000	...	...	...
1971	79,000,000	8,830,000	203,000,000	21,570,000	0.390	0.410
1973	86,000,000	...	...	...	...	...





Source U.S. Bureau of Mines, The Boston Consulting Group, PCA Market Research Dept.

FIGURE 2-12 (a) Cement Shortage - Capacity vs Consumption [107]



*Rated gray cement capacity in millions of barrels.
Return on Net Worth data published by First National City Bank.

FIGURE 2-12 (b) Cement Shortage - The Return on Capacity [106]

FIGURE 2-12 CEMENT SHORTAGE

million tons. Since much information about portland cement and its properties and utilization is available in the literature, a detailed description is not required here. However, energy consumption in cement manufacturing processes has not been well documented and more detail on this aspect will be given in later sections.

The chemical composition of portland cement has a very narrow range between different manufacturers. As shown in Table 2-21, lime, silica and alumina are the major constituents making up 90% of the total. For comparison purposes the other cementing materials are included in Table 2-21 and will be discussed in the following sections.

Most of the chemical components exist as compounds in the end product of the cement manufacturing process. The major compounds found in portland cement are shown in Table 2-22, with percent proportions for each main type of cement. This table has been included since there have been recent changes in the specification types for Canadian portland cement. The gradation properties of portland cement are given for comparison purposes in Figure 2-6.

The chemistry involved in the manufacturing of portland cement is extremely complicated, but some simplified concepts will be given here to indicate similarities with other types of cement. The main raw materials for portland cement are limestone (for calcareous components) and clay (for silica and alumina). These raw materials are dissociated during the manufacturing process (which is discussed later) in the following manner:

$$\text{limestone} \rightarrow \underset{\text{(lime)}}{CaO} + \underset{\text{(carbon dioxide)}}{CO_2}$$

TABLE 2-21

COMPARISON OF TYPICAL CHEMICAL COMPOSITIONS (%)

PRINCIPAL CONSTITUENTS		PORTLAND CEMENT (a)	FLY ASH (PFA) (b)	BLAST FURNACE SLAG (c)	STEEL SLAG (BOF) (d)	STEEL SLAG (OH) (e)
Lime	CaO	60-65	1.1-5.4	36-45	41.3	25.8
Silica	SiO_2	70-24	45-51	33-42	15.6	16.[illegible]
Alumina	Al_2O_3	4-8	24-32	10-16	2.2	2.4
Ferric Oxide	FeO or Fe_2O_3	2-5	7-11	0.3-2.0	20.0	26.0
Magnesia	MgO	0-5	1.5-4.4	3-16	6.9	10.0
Manganese Oxide	MnO	...	...	0.2-1.5	8.9	11.2
Sulphur	S	...	...	1.0-3.0 (e)	...	...
Sulphur Trioxide	SO_3	1-3	...	...	...	...
Titanium Oxide	TiO_3	...	...	...	0.5	0.8
Alkali Oxide	Na_2O, K_2O	...	...	...	...	...
Free Calcium Oxide		...	...	...	3.3	2.1

(a) From [67]
(b) From [9]
(c) NSA
(d) By STELCO Research and Development Dept.
(e) Principally in the form of Calcium Sulphide

TABLE 2-22

CHEMICAL COMPOUNDS IN PORTLAND CEMENT

NAME OF COMPOUNDS	FORMULA	AMERICAN ASTM (a)			
		TYPE OF CEMENT			
		I	II	III	IV
Major Compounds		%	%	%	%
Tricalcium silicate	$3CaO.SiO_2$	53	47	58	26
Dicalcium silicate	$2CaO.SiO_2$	24	32	16	54
Tricalcium aluminate	$3CaO.A\ell_2O_3$	8	3	8	2
Tetracalcium alumino ferrite	$4CaO.A\ell_2O_3.Fe_2O_3$	8	12	8	12
Minor Compounds					
Gypsum	$CaSo_4.2H_2O$	...	...	...	...
Magnesia	MgO	...	...	...	...
Alkali oxide	$Na_2O.K_2O$	...	...	...	...

(a) From [55]

$$\text{clay} \rightarrow SiO_2 + Al_2O_3 + Fe_2O_3 + H_2O$$

(silica) (alumina) (ferric oxide) (water)

These processes take place in a kiln and require substantial energy (> 90% of total energy for cement production).

The portland cement is hydrated with water in the various concrete mixes emitting heat. The actual hydration chemistry is very complex and not fully understood at the present time. The simplified hydration processes and their contributions to strength gain are shown in Table 2-23.

The major cementing properties are probably derived from the formation of tobermorite gel from the hydration of tricalcium silicate and dicalcium silicate, comprising about 80% of the total cement. Minor constituents that are important contributors to concrete properties in specific conditions are: gypsum; alkalioxides; and magnesia. The gypsum reacts with the calcium aluminate and prevents the formation of hydrated calcium aluminate and precipitates as an insoluble, water-rich compound, calcium-sulphur-aluminate. Too much gypsum results in undesirable expansion and a hardened paste of lowered strength. If additional sulphate is introduced into the system (typically from groundwater) as the portland cement hydrates, additional gypsum is produced and a potentially harmful sulphate attack occurs by the following reaction:

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2$$

Alkalioxides (Na_2O, K_2O) have no positive rate, but can react with certain aggregates to cause alkali-silicate or alkali-carbonate reactions resulting in deleterious expansion of concrete. The higher content of magnesia leads to long term unsoundness because of its very slow hydration, accompanied by expansion, of free MgO crystals (periclase) when these are above

TABLE 2-23

HYDRATION OF PORTLAND CEMENT AND CONTRIBUTION TO STRENGTH

PARTS	HYDRATION			CONTRIBUTION TO STRENGTH
1	$2(3CaO\cdot SiO_2)$ (tricalcium silicate)	$+\ H_2O$ (water)	$=\ 3CaO\cdot 2SiO_2\cdot 3H_2O\ +\ 3Ca(OH)_2$ (tobermorite gel) (calcium hydroxide)	early age strength continue but decreasing effect (a)
2	$2(2CaO\cdot SiO_2)$ (dicalcium silicate)	$+\ H_2O$	$=\ 3CaO\cdot 2SiO_2\cdot 3H_2O\ +\ Ca(OH)_2$	little contribution up to 28 days largely later increase
3	$4CaO\cdot A\ell_2O_3\cdot Fe_2O_3$ (tetracalcium alumino ferrite)	$+\ 10H_2O\ +\ 2Ca(OH)_2$	$=\ 6CaO\cdot A\ell_2O_3\cdot Fe_2O_3\cdot 12H_2O$ (calcium alumino ferrite hydrate)	not clear probably little at any time
4	$3CaO\cdot A\ell_2O_3$ (tricalcium aluminate)	$+\ 12H_2O\ +\ Ca(OH)_2$	$=\ 3CaO\cdot A\ell_2O_3\cdot Ca(OH)_2\cdot 12H_2O$ (tetracalcium aluminate hydate)	up to 28 days and diminishing thereafter
5	$3CaO\cdot A\ell_2O_3$	$+\ 10H_2O\ +\ CaSO_4\cdot 2H_2O$ (gypsum)	$=\ 3CaO\cdot A\ell_2O_3\cdot CaSO_4\cdot 12H_2O$ (calcium mono sulfo aluminate)	affecting the setting time (b)

(a) contributes 80% of total
(b) only retarders, rest accelerators

a certain size. The degree of unsoundness depends on the crystal size since the smaller crystals tend to hydrate more rapidly or without setting up excessive internal pressures.

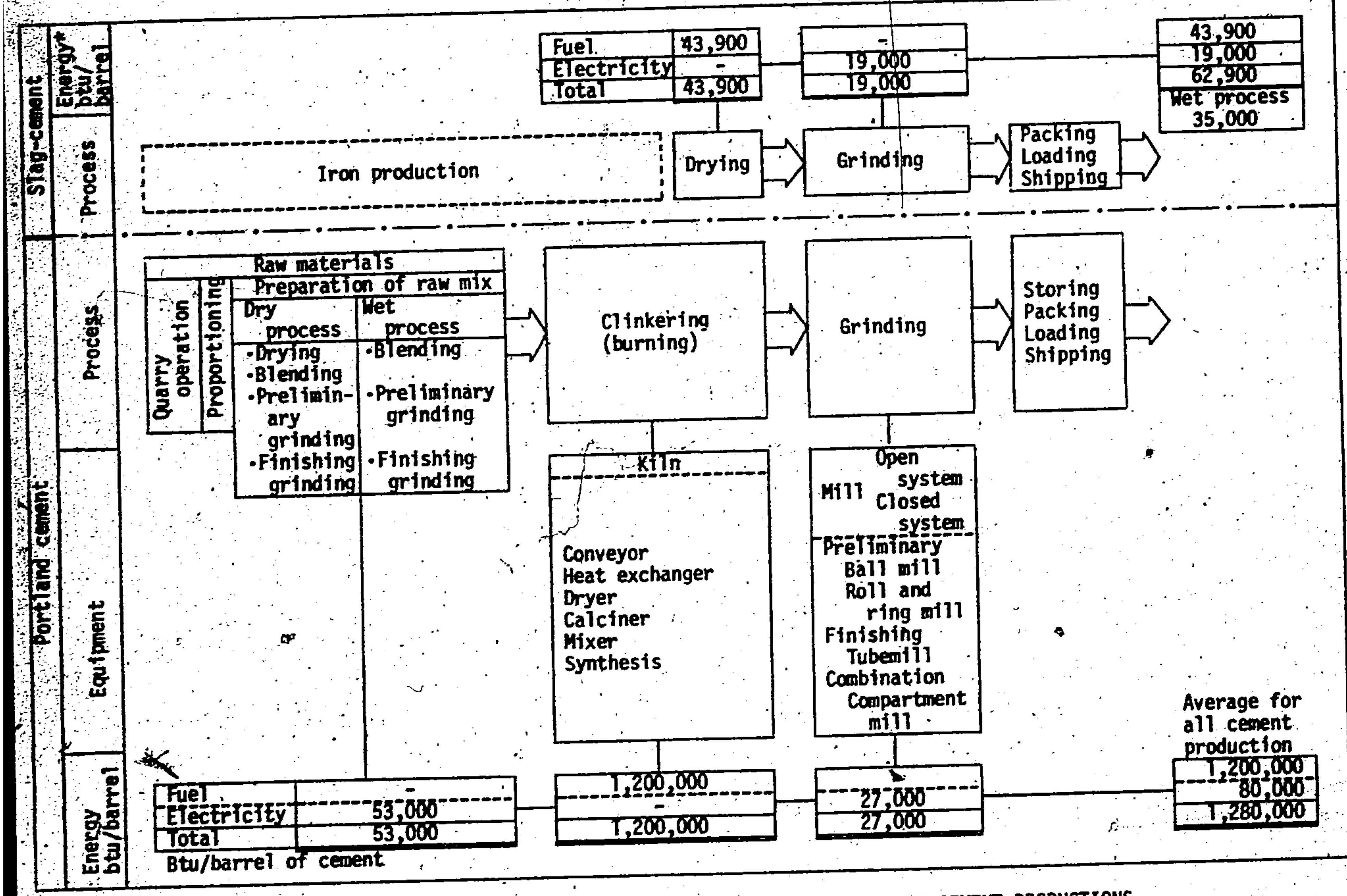
Manufacture of Portland Cement

The manufacturing of portland cement is divided into two main processes: blending and clinkering (or calcinating) the materials to the desired composition of controlled temperatures; and grinding the resulting clinker to optimum fineness followed by final packing and shipping. The important factors affecting the final product's quality are the proportions of constituent chemical compounds, temperature of clinkering and fineness of grinding.

The clinkering process and the grinding process utilize the most energy in portland cement manufacturing. Thus, the efficiency of these processes largely influences the unit production cost of cement (for instance, kilns are generally very inefficient). Schematic flow charts comparing portland cement production to slag cement production are shown in Figure 2-13.

Fuel Consumption in Portland Cement Manufacture

The flow charts in Figure 2-13 show the processes, equipment (including functions) and average (wet and dry process) energy requirements for cement manufacturing. The main areas of interest are the clinkering and grinding processes which use most of the energy. The temperature in the kilns, which are mainly of the rotary type, ranges from 2500°F to 2900°F. The heat for holding this desired temperature is supplied by coal, oil, gas or combinations of these fuels.



*Calculation is shown in Appendix 2-4

FIGURE 2-13 SCHEMATIC FLOW CHARTS OF PORTLAND CEMENT AND SLAG CEMENT PRODUCTIONS

Canadian cement plants (all based on the wet process) in 1971 operated a total of 57 kilns [43] using coal (9% of total energy consumption based on cost), oil (35%), gas (26%) and electricity (30%) for heating. In 1972 [95], there were 469 kilns operated by the 169 active U.S. cement plants (106 wet process; 63 dry process).

The temperatures required for the formation of various compounds in the kiln are summarized in Table 2-24 in increasing order. Theoretical temperature requirements for converting the raw mixture to cement clinker in the kiln are given in Table 2-25. The total heat requirement in terms of British thermal units (Btu) for the clinkering process varies with: the basic method, i.e., wet process or dry process; original water content of raw materials; kiln type; and kiln efficiency. Typical theoretical heat requirements are shown in Table 2-26. Heat losses in the kiln are reported to be about 76% as shown in Table 2-27. The actual heat supplied in the kiln as reported by several investigators [22] is summarized in Table 2-28.

A study of 176 active cement plants in the U.S. in 1960 indicated an average heating requirement of 1.31 million Btu for each barrel of cement produced [70]. Blanks [10] has assumed the very wide range of 700,000 to 1,700,000 Btu heat required indicating the heavy dependence on the various factors mentioned previously.

It can be shown by using the data on fuel consumed and cement produced [75] (all by the wet process) that an average of about 840,000 Btu per barrel of cement produced (based on the conversion units of Appendix 2-3) was used by Canadian cement manufacturing plants in 1971.

TABLE 2-24

TEMPERATURE AND COMPOUND FORMATION IN KILN [67]

TEMPERATURE		PRODUCED COMPOUNDS
°F	°C	
212	100	Free water evaporated
300-600	150-350	Loosely bound water evaporated
930	500	Firmly bound water evaporated
1110	600	$MgCO_3$ decomposed
1650	900	$CaCO_3$ decomposed
2280	1250	Some liquid formed
2330	1280	Major compound formed
2500-2900	1400-1600	Clinker

TABLE 2-25

TEMPERATURE REQUIREMENTS

PROCESS		TEMPERATURE (°F)
1	Evaporation of the water of the mixture	930
2	Decomposition of the clay	≈1000
3	Dissociation of sulphates	≈1000
4	Dissociation of carbonates	1650
5	Heating the mix to clinkering point	2500 to 2900

TABLE 2-26

THEORETICAL HEAT REQUIREMENT IN KILN [22]

(Btu per barrel)

PROCESS		DRY	DRY	SEMI-WET	WET
Water Content in mix (%)		2.5	2.5	30	60
Temperature at stock-gas (°F)		1,500	1,000	800	450
Kiln	1 Evaporation of water	23,367	21,079	365,000	1,113,840
	2 Decomposition of the clay	unknown (probably small amount of heat)			
	3 Dissociation of the sulphates	3,402	3,402	11,340	11,340
	4 Dissociation of carbonates	369,488	369,488	369,488	369,488
	5 Heating the mix to clinkering point	this heat already included in 3 and 4			
	Total Heat	396,257	393,969	746,478	1,494,668
Coal*	Coal theoretically necessary (lb/barrel)	30	30	57	114
	Coal actually used (lb/barrel)	120	85	115	150

* Equivalent heat is calculated using the conversion table of Appendix 3.

TABLE 2-27

HEAT LOSS IN ROTARY KILN [22]

LOSS	PERCENT
Heat utilized	23.57
Heat loss in clinker	13.07
Heat loss in stack-gases	53.43
Heat loss in radiation	7.72
Minor loss	2.21
Total heat supplied in kiln	100.00

TABLE 2-28

TOTAL HEAT SUPPLIED IN KILN [22]

(Btu per barrel of clinker)

INVESTIGATORS	HEAT	PROCESS	KILN TYPE
Richards	1,850,815	possibly wet	rotary
Carpenter	1,476,370	"	"
Helbig	1,382,118	"	"
Newberry	1,474,000	wet	"

Electric Power

The processes related to electric power include grinding the raw materials and clinker, and possibly all other processes excluding most of the quarry operations. Obviously, at present the cost of electric power precludes its use in kilns which are the main energy users. The electric power is mainly supplied from outside of the cement manufacturing plants, but in some cases power is generated within the plant. The requirements for electric power also vary with the processes used in handling the raw materials. The total electric energy used in cement plants in the U.S. and Puerto Rico in 1960 is shown in Table 2-29. The average electric energy consumption is 23.3 Kwh per barrel of cement or 80,000 Btu per barrel. It can be found that there is no significant difference between the wet process and dry process in electric energy consumption per pound of cement produced. This can be contrasted to the large difference in total energy requirements between the wet and dry processes.

In Canada in 1971, total electric energy of 1,154,201,849 Kwh was used in the production of 9,034,226 tons or 47,700,000 barrels of cement [75]. This figure gives 23.5 Kwh per barrel of cement, being very close to U.S. average of 23.3 Kwh per barrel.

This total electric energy use may be distributed approximately into three parts [70]:

one-third for grinding the raw materials;
one-third for grinding the clinker; and,
one-third for all other purposes.

TABLE 2-29

ELECTRIC ENERGY USED IN CEMENT PLANTS IN U.S. AND PUERTO RICO IN 1960 [70]

PROCESS	TOTAL ELECTRIC ENERGY USED (Kwh)	%	FINISHED CEMENT PRODUCED (Barrel)	ELECTRIC ENERGY (Kwh/Barrel)	REMARKS (Btu/Barrel)
Wet	4,152,000,000	55.9	186,370,000	22.3	76,000
Dry	3,274,000,000	44.1	132,639,000	24.7	84,000
Total	7,426,000,000	100.0	319,009,000	23.3	80,000

When the equivalent 80,000 Btu per barrel of cement for electric power is compared with the total 1,200,000 to 1,300,000 Btu for all energy requirements on an equivalent heat energy basis, the electric energy does not appear to be an important factor in cement manufacturing. However, when a comparison is made on a cost basis, a far different conclusion can be drawn. An analysis of the energy consumption for Canadian cement production in 1971 as indicated in Table 2-30 shows that the fuel consumption of 840,000 Btu per barrel of cement is much lower than the U.S. average of 1.3 million Btu, and it can be found that the fuel unit cost of $0.48 per one million Btu is much lower than the electric unit cost of $2.18 per one million Btu. However, there may increasingly be many limitations on using the cheaper fossil fuel energy sources instead of electric energy in cement manufacturing due to rapid changes in the relative economics with the energy crisis, environmental controls, the move to more nuclear power, utilization of solid wastes in thermal generating plants and cement kilns, etc.

The total energy requirement of 922,000 Btu per barrel of cement in Canada is considerably lower than the average of 1,280,000 Btu indicated in Figure 2-13.

Utilization of Granulated (or Pelletized) Blast Furnace Slag

When granulated blast furnace slag is utilized in cementitious type slag-cement manufacture, its processing is essentially reduced to drying and grinding the slag. The elimination of the clinkering process which requires about 94% of the total energy in portland cement manufacture is possible because the slag has already been treated during the iron manufacturing processes as mentioned before, i.e. the slag has "locked" in a

TABLE 2-30

ENERGY ANALYSIS FOR CEMENT PRODUCTION IN CANADA

(Calculated from [76] data and Appendix 2-3 Energy Conversion Table, and based on the total production of cement, 9,000,000 tons or 47,700,000 barrels in 1971)

ENERGY		UNIT	QUANTITY	COST (CANADIAN $)	%	EQUIVALENT Btu IN MILLION	%	Btu PER BARREL OF CEMENT			UNIT PRICE PER MILLION Btu
								FUEL	ELECTRICITY	TOTAL	
Fuel	coal	ton	181,400	2,562,000	9	4,800,000	11	840,000	...	840,000	0.48
	oil	Imp. Gallon	107,704,000	9,507,000	35	15,500,000	35				
	gas	M cu.ft	21,700,000	7,316,000	26	19,500,000	45				
Electricity		Kwh	1,154,000,000	8,509,000	30	3,900,000	9	...	82,000	82,000	2.18
Total		...	...	27,894,000	100	43,700,000	100	...	...	922,000	...

large amount of energy acquired during the iron manufacturing process. The unit grinding energy for slag, 19,000 Btu per barrel, is lower than the 27,000 Btu per barrel for portland cement because of the granulated nature of the slag. This advantage from an economic viewpoint was emphasized in an Ontario Hydro Report [18] and others. The total energy requirements for slag cement production is estimated as 62,900 Btu per barrel as shown in Figure 2-13. An example of the cost analysis for slag cement manufacture is shown in Appendix 2-4.

The utilization of slag, which may even be wasted, as a cementing material in pavements, structural concrete, masonry unit and other purposes has multi-beneficial effects; lowered production cost of iron; energy savings; mineral resource conservation; and, many environmental enhancement factors.

2-3-1-2 Metallurgical Cements [18,49]

The terminology "Metallurgical Cements" should be clarified in order to avoid any confusion in what follows. The slag-cement already mentioned is only one of the many metallurgical cements. All the cementing materials based on hydraulic setting properties, other than portland cement, are designated by the American Society for Testing and Materials to be "Metallurgical Cements". The main types of metallurgical cements are given in Table 2-31.

These types of cement are widely accepted in Europe [18]. Thus in Europe portland cement represents only one of the number of cements in common use whereas in North America portland cement is essentially the only cement used in concrete construction. There is no metallurgical cement currently available commercially in Canada. Of the various kinds of metallurgical cements, slag-cement is the prime concern in this thesis because this cement is closely related to the utilization of secondary products and the efficient use of energy. The slag-cement made from pelletized slag which has cementing properties that are discussed in detail later, has certain advantages or disadvantages in common properties as indicated in Table 2-32.

While the characteristics of slags depends on many factors, one of the most uncontrollable factors is a dependence on the production of iron since granulated or pelletized slags are secondary products of little concern to primary producers. Thus a consistent and continuous supply with the desirable chemical composition cannot be guaranteed because output and chemical composition are controlled by the amount and quality of iron.

TABLE 2-31

TYPES OF METALLURGICAL CEMENTS [10,18,22,43,47]

TYPE	ACTIVATOR AND BLENDED MATERIALS	PROPERTIES
Slag-cement	slag* + hydrated lime	Light colour. Specific gravity 2.6-2.8. For more details see Table 2-29.
Portland blast furnace cement	portland cement + slag	Cost reduction. Low heat generation. Absorption of released lime from hydration of p.c. Less shrinkage. Lighter colour. Specific gravity 3.0-3.15. Higher resistance to chemical attacks.
Supersulphate cement	calcined gypsum + slag + small amount of portland cement or lime	Slag 80-85%. $CaSO_4$ 10-15%. Lime or p.c. in 2% composition. Higher resistance to sulphate exposure and dilute acid attack. Fineness 4980 cm^2/gr (Blaine). Lower water required for given consistency. Higher strength in water-curing. Lower heat generation.
Expanding cement	portland cement + sulpho-aluminous cement + slag	Up to 5% expansion under moist condition. Used for special purposes: repair work; casting of crown section of arches; foundation work; anchorage; pavements; dams.
Pozzolanic cement	portland cement + pozzolan	Pozzolan constituent is between 15 and 40% of total weight. Higher silica or higher silica:alumina ratio, greater resistance to sulphate attack. Absorption of lime released from hydration of p.c. Higher ultimate strength, low early strength. Lower heat generation.
Purdon cement	slag + common salt + small amounts of lime or portland cement	Performance is similar to slag-cement. (available information limited).

*Slag means vitrified blast furnace slag.

TABLE 2-32

MAIN PROPERTIES OF SLAG CEMENT [10, 18, 22]

RELATIVE ADVANTAGES OVER PORTLAND CEMENT	RELATIVE DISADVANTAGES OVER PORTLAND CEMENT
Lower heat generation during hydration	Slower initial development of strength (Not always the case)
Higher ratio of tensile to compressive strength	Unsoundness when exposed to air
Lower shrinkage	Aging effect in storage
Higher resistance to chemical attacks	Weak in mechanical wear
Tougher and less brittle	
High resistance to seawater attack	

This is the main barrier to the growth of slag-cement utilization in addition to the superiority of portland cement in several aspects as indicated in Table 2-32. Since the early days of this century the demise of the slag-cement industry in North America has not been too much because of the properties of slag-cement itself but because of the production and quality problems.

The specifications for portland cement in Canada and the U.S. are shown in Table 2-33 for convenience.

TABLE 2-33

GENERAL PORTLAND CEMENT SPECIFICATIONS IN CANADA AND U.S.

DESCRIPTION		CANADA	U.S.
Designation		CSA Standard A5-71	ASTM C150-70
Type		10 Normal Portland Cement 20 Moderate Portland Cement 30 High Early-Strength Portland Cement 40 Low Heat of Hydration Portland Cement 50 Sulphate Resistant Portland Cement No Air-Entraining Cement	I and IA (general use) II and IIA III and IIIA High Early-Strength IV Low Heat of Hydration V Sulphate Resistance A: Air-Entraining Cement
Chemical requirement		General requirement No optional requirement	1. Standard chemical requirement 2. Optional chemical requirement
Physical requirement		Fineness Soundness Sulphate resistance Time of setting Heat of hydration Compressive strength No optional requirement	1. Standard physical requirement Air content of mortar Fineness Soundness Strength Time of setting 2. Optional physical requirement False set Heat of hydration Strength Sulphate expansion
Packing	Bag	80 pounds (36.3 kg) net	94 pounds (42.6 kg) net
	Bulk	Short tons unit of 2000 lb. (0.9 metric ton)	Barrel 376 pounds (170.6 kg)

2-3-2 Granulated Slag Fines

In this chapter, granulated or pelletized slag fines are used with slag fines or slag cement synonymously.

Historical trends in using slags as cementing material

Loriotin first observed and studied the cementing properties of blast furnace slag (called slag hereafter) in 1784 [18], and in 1862 Emil Langens discovered that granulated slag has cementing properties when mixed with lime [18]. It is reported that the first slag-lime cement was produced commercially in Germany in 1865 [43]. Since that time, investigations of the properties of slag cements have been carried out by Michaëlis, Prüssing, Tetmajer, Prost, Feret, and Grün amongst many others [43]. In 1883, slag was used as one of the raw materials for portland cement manufacture. The first production of portland blast furnace type cement, produced by grinding together portland cement clinker and granulated slag was in Germany in 1892 [43].

Edwin C. Eekel considered slag-cement as a most important member of the group of pozzolan cements [22]. Most investigations [43, 10], have pointed out that ground granulated slag does not set if it is mixed with water. On its own, ground slag is not a cement, it has to be activated and this is done by means of lime in slag-cements as specified in the ASTM standards, portland cement in portland blast furnace cement or by portland cement and calcium sulphate (gypsum) in supersulphate cement (Table 2-31).

It should be noted that granulated slag is not a pozzolan and its hydraulic reactions are specific with the formation of direct hydrated compounds whereas the pozzolans such as volcanic ashes and fly ash react with lime in a different way and require a much larger quantity of lime for cementing reactions than slags do. The early confusion between the slag-cements and pozzolans such as in Eekel's grouping still exists since the early slag-cements were activated by limes [32,18].

The slag is used in two general ways in cement manufacture: either it is one of the raw materials from which portland cement clinker is made; or, its inherent hydraulic properties are utilized independently or by mixing with other constituents. Recent ASTM standards classify blended hydraulic cements as portland blast furnace slag cement, portland-pozzolan and slag-cement with subclassifications according to their combination with air-entraining agents. The slag cement in ASTM classifications belongs to the latter type of utilization indicated above, whereas portland blast furnace slag cement produced by intergrinding the granulated slag and portland cement clinker belongs to the former type of utilization.

Cementing value of granulated slags

When the molten slag from the blast furnace goes through a quick cooling process as indicated in the previous chapter, it solidifies forming isotropic transparent glassy slag, some of which shows under microscope examination or other techniques, described later, brown or black zones where incipient crystallization has set in. Amorphous glassy slag is more "energetic" in reaction as a cementing material than slowly cooled crystallized slag because it has lost no latent (internal) energy through crystallization [38] [93]. As indicated previously, although ground slag fines activated by some optimum amount of lime develop higher strength, ground slag fines alone show considerable strength gain, often enough for specific end uses. For example, a naturally cemented mass of granulated slag fill placed in 1911 and removed in 1948 indicated some cementing properties [38]. (This is undoubtedly due to the presence of some lime in the slag from the blast furnace.)

The cementing properties of the granulated slag are contributed by many factors. The predominant factors and interrelation between these have been extensively discussed in the literature [10, 18, 22, 32, 38, 41, 43, 47, 49, 50, 60, 76]. The temperature history of the slag before and during the cooling or granulating and granulation (or pelletizing) process mainly relates to the glass formation. This factor, and the chemical composition of the slag, the fineness of the ground products, and their age dependance with storage will be discussed separately.

Each discussion will include details concerning evaluation methods for the hydraulic properties, and correlations to other factors. Usually these evaluation methods are verified by the determination of strength development of mortar specimens or appropriate mix specimens under various preparation and curing conditions.

It has been recognized for some time that the hydraulic hardening potential increases or decreases proportionally with the amount of glass formed in the slag. The higher the total glass content in the granulated slag, the more hydraulic properties the slag will exhibit. The "total glass content" rather than "glass content" is used purposely because not all of the glass contributes to the strength development as will be indicated later when ultra-violet testing is discussed. The importance of high glass content to the strength development is the most important reason for the slag to be granulated or pelletized with high glass content, processes that often involve additional costs. In addition to the purely physical result such as grain shape, specific gravity, etc., the granulating has two important chemical effects: one being to make the slag energetically hydraulic if it has a suitable chemical composition [10, 18, 22, 38, 43, 47, 60, 76, 93]; the other being to remove a portion of the sulphides contained in the slag in the form of hydrogen sulphide (H_2S) [18, 22, 43, 58]. This H_2S generation obviously must be controlled and suitable equipment is available and has generally been installed for its control. The hydraulic properties of the granulated slag are due to the presence of a silica-alumino-ferrite of calcium ($3CaO.A\ell_2O_3.2SiO_2$). This compound appears also in portland cements, but in this case it is entirely inert, owing to the slow cooling it has undergone. However, in the case of granulated slag which is cooled suddenly, it becomes an important hydraulic agent [22].

The granulated slag combines particularly with hydrated limes in setting, and gives rise to silicates and aluminates of lime identical with those which are formed by entirely different reactions during the setting of portland cement as indicated in Table 2-23. Temperature can have an effect on the glass structure of the molten slag during the formation of slag. Slags which have a low CaO/SiO_2 ratio (less than 1.3) and are obtained at relatively high temperatures possess a better strength development than slags which have CaO/SiO_2 ratios of 1.3 or larger and are produced at lower temperatures [60].

Lea has explained the mechanism of glass formation as the rearrangement of the ions which induces the "clear orientation" in the crystals during the passage from the liquid state of molten slag to a crystalline solid condition such as air-cooled slag [43]. The viscosity of the molten silicates near their freezing point is so large that this rearrangement only occurs slowly. However, if the cooling is rapid as in the case of granulation or pelletization, the ionic groups largely retain their irregular arrangement, and with the viscosity increasing rapidly as the temperature falls, the slag passes from the liquid state to one in which the rigidity approaches that of a solid. This occurs without the development of a crystalline structure. Below the freezing point of the crystallized mix, the completely crystallized solid is stable, but the glass behaves as a greatly undercooled liquid having a very high internal viscosity which is unstable and tends to change into the crystalline state. This tendency is actually restrained by the high viscosity which reduces the mobility of the constituent ions.

The ease of the granulation or pelletization of glassy materials depends on the chemical composition of the slag and on the temperature at which it comes out of the furnace. Siliceous slags cool to glasses more easily while those of high lime content are more difficult to prevent from crystallizing [43]. However, higher lime slags are preferable for the manufacture of granulated or pelletized slag because of their greater activity as cementing materials. An increase in the temperature of the molten slag when granulated promotes the hydraulic properties of the products. Thus, there is an optimum glass content-lime content granulated or pelletized slag for hydraulic properties. It has been reported that there exists a roughly linear relationship between glass content and strength, indicating that increasing the content of crystalline compounds reduces the cementing properties although some of the crystalline compounds may actually make some contribution to strength [43].

Pure synthetic glasses can be examined for their hydraulicity. The test results on such ground glasses of alkermanite by Keil, Butt and Budnikov are not concordant [47]. But, in the presence of activators this synthetic glass of the CaO-$A\ell_2O_3$-SiO_2-MgO system and commercial slag glasses behave similarly [47]. It may well be that the temperature of the preparation of the glass, as is the case in slag cooling also has some influence, but the importance of lime shows up clearly. The fineness of grinding of these glasses and slags was not considered.

High temperature effects on the unstable irregularity of the glassy state were explained with regard to the relative potential forces of ions restrained by high viscosity at sudden cooled states by Lea [43]. Schroeder [60] indicated that granulation of molten slag heated well above the liquidus temperature determines the degree of deformation of the silica network and its transformation into a solid state.

The activity of granulated slag must be related to the structure of the glass and the ease with which hydration can occur [32, 43, 60]. The two main theories with which theoretical considerations of the behaviour of the ground slag are connected are Zachariasen's network theory by which glass constituents can be divided into two glasses, that is, network formers and network modifiers [43]; and, the crystalline theory by which the glass structure contains small regions of crystalline order containing most of the metal cations, linked together by an amorphous region formed by the residual anions [43]. Schroeder quoted the suggestion of J. Cleret de Langarant that the structure of the glass in the slag may be related to the hydraulic properties. He further concluded from his test results that the slag grains contain various kinds of glass of different hydraulic characteristics. In order to separate the different types of grains, the ultra-violet test was used as indicated in Appendix 2-1, because different types of glass will emit different luminescent colours. The German Research Institute developed this test technique and first applied it to the evaluation and comparison of granulated slags [60]. Grains which had pink radiation colours developed the highest strength, whereas the yellow, grey-brown and blue radiation colours had lower strength development. The crystalline inclusions, also of blue and violet, developed little strength which is assumed to be due to their low glass content. This ultra-violet technique of separating the different glasses is considered to improve the total glass content obtained by conventional microscope techniques as described in Appendix 2-2 and decrease the uncertainty of the formulae methods of the evaluation of hydraulicity. More work is needed on these methods of analysis, and at present, hydraulic properties cannot be adequately predicted on the basis of the theories of network and crystalline behaviour.

A formula for predicting the strength of slag-cement at 90 days was given by Paker and Nurse, relating strength to the glass content (conventional total glass content) and basicity [32].

$$(S90 - 75) = 0.38\,(M - 0.72)\,G \qquad (2\text{-}1)$$

where: S90 = the 90 day strength of a 1:2:4 concrete of w/c radio 0.60 and assuming a mixture of 65% ordinary portland cement 35% slag cement;

$$M = \text{basicity} = \frac{CaO + MgO + \frac{1}{3} Al_2O_3}{SiO_2 + \frac{2}{3} Al_2O_3} \qquad (2\text{-}2)$$

or modulus for potential activity of slag; and,

G = % glass content determined by a microscope analysis.

The simple product GM was adopted as a guide to the activity of a slag, where the definitions of G and M are the same as above. The higher the value of GM, the more hydraulic the slag provided that M has a value between 0.72 and 1.50. At lower values of M, the slag has no hydraulic activity, and above 1.5 the slag cannot be granulated without devitrification (crystallization) occurring [43].

It was indicated by test results [43, 60] that by simple multiplication of the glass content (as determined by the ultra-violet test) with the CaO/SiO_2 ratio, a linear relationship exists with the strength values.

$$\text{Strength} = G'M' \qquad (2\text{-}3)$$

where G' = glass content by ultra-violet test

M' = Basicity (= CaO/SiO_2)

These three formulae, Equations 2-1 to 2-3, indicate that neither a composition modulus (M or M'), nor glass content (G or G') are sufficient to characterize the hydraulic properties of a slag.

The chemical composition of granulated slag affects its potential hydraulic properties. It has been considered that the expression of basicity, rather than the amount of individual compounds in the slag, is a satisfactory measure for the hydraulic hardening capacity. A number of empirical formulae based on chemical analysis (which is a routine part of the control procedures in iron production) have been developed. The simplest formulae for hydraulic evaluation are the CaO/SiO_2 and $A\ell_2O_3/SiO_2$ ratios. The hydraulic value increases with an increase in both of these ratios [22, 38, 43, 51, 60], up to a limiting point when increasing CaO content makes granulation (or pelletization) to a glass difficult [43]. However, it has been indicated [38] that crystallization proceeds rather slowly in slag high in silica and more rapidly and completely in those high in lime and magnesia. This is consistent with Lea's explanation [43]. Many other formulae have been suggested for evaluation purposes. Most of these formulae consider two or three main compounds, usually CaO, SiO_2 and $A\ell_2O_3$ as comprising about 95% of the total slag, in the formulae.

All of these formulae methods are based on the assumption that the glass content effects are constant and "homogeneous". This three component system is widely used by various authorities. The first formula for this chemical composition criterion is: [10, 18, 38, 43, 47]

$$\frac{CaO + MgO + \frac{1}{3} A\ell_2O_3}{SiO_2 + \frac{2}{3} A\ell_2O_3} \geq 1.0 \qquad (2\text{-}4)$$

This formula appears in a tentative ASTM specification (C205-48T) which disappeared in the amendment to ASTM C595-72, and was adopted for granulated slag to be ground with portland cement in Germany.

The second formula is: [43] [93]

$$\frac{CaO + MgO + A\ell_2O_3}{SiO_2} \geq 1.0 \qquad (2\text{-}5)$$

The third formula is : [43]

$$\frac{CaO + CaS + \frac{1}{2} MgO + Al_2O_3}{SiO_2 + MnO} \geqq 1.5 \qquad (2\text{-}6)$$

The fourth formula, which is used in France, is termed "the index of quality" [43]:

$$i = 20 + CaO + Al_2O_3 + 0.5MgO - 2SiO_2 \qquad (2\text{-}7)$$

In applying this index of quality, and inserting percentage weight contents into it, the hydraulic properties of slag are classified as follows:

Inferior if $i<12$; and

very good if $i>16$

In comparing these formulae, attention is drawn to the role of Al_2O_3 and MgO. The Al_2O_3, for instance, is either evaluated as a basic or acidic component, or it is considered simultaneously as an acidic and basic activator. Formula (2-4) indicates that MgO is as effective as CaO in producing hydraulic properties in a slag. Some workers have found that up to contents of about 10% MgO, the hydraulic value of granulated slag is not affected adversely due to volume increase, and the effect of Al_2O_3 is considered to be on the unfavourable side. Formula (2-5) is derived from evidence that an Al_2O_3 content of about 12% or more is advantageous. This formula appears in the specification DIN 1164 (1967) in Germany replacing Formula (2-4). The Cemsave Cement Company [93] in the U.K. uses this formula as their standard. The slag from the pelletizer at DOFASCO was evaluated by each of the above formulae (using the chemical analysis from the supplier) as shown in Table 2-34 for comparison purposes.

TABLE 2-34

CALCULATED MODULUS FOR SLAG

A CHEMICAL COMPOSITION OF BLAST FURNACE SLAG [23]

COMPONENTS	PERCENT
CaO	38.60
SiO_2	34.90
Al_2O_3	10.00
MgO	13.70
FeO or Fe_2O_3	0.64
MnO	0.19
CaS	Not determined

This data is from the analysis of air-cooled slag for Modulus calculation.

TABLE 2-34 (Continued)

B INDEX CALCULATION

	FORMULA	INDEX	EVALUATION
2-3	$\dfrac{CaO+MgO+\frac{1}{3}A\ell_2O_3}{SiO_2+\frac{2}{3}A\ell_2O_3} \geq 1.0$	1.3	✓
3	$\dfrac{CaO+MgO+A\ell_2O_3}{SiO_2} \geq 1.0$	1.8	✓
4	$\dfrac{CaO+CaS+\frac{1}{2}MgO+A\ell_2O_3}{SiO_2+MnO} \geq 1.5$	(a) 1.6	✓
5	$i = 20+CaO+A\ell_2O_3+0.5MgO-2SiO_2$	5.6	Inferior
...	$\dfrac{CaO}{SiO_2}$	1.1	...
...	$\dfrac{A\ell_2O_3}{SiO_2}$	0.29	...
...	GM	57 (b) 117 (c)	

(a) CaS is not counted in this index calculation.

(b) Value 57 is based on glass content G = 45%.

(c) Value 117 is based on glass content G = 90%.

One of the attempts to explain the chemical composition of slags and other cementing materials is shown by the composition ternary diagrams [22] [38] in Figure 2-14 (a) and tetrahedron diagram [47] in Figure 2-14 (b). In the ternary diagram, the relative location is expressed by the SiO_2 - CaO - $A\ell_2O_3$ system whereas in the tetrahedron diagram it is expressed by the SiO - CaO - $A\ell_2O_3$ - Fe_2O_3 system, these oxides being the major constituent of these materials. DOFASCO blast furnace slag and Ontario Hydro Lakeview fly ash are shown in the ternary diagram of Figure 2-14 (c).

Sometimes, direct strength tests on specimens which are mixed in various desirable combinations give more reliable hydraulic value data than formulae. This method for testing the hydraulic or pozzolanic reactivity is given in ASTM C595-72 in terms of the "pozzolanic activity test". Lea [43] introduced Keil's recommendation on the "Hydraulic Index" for assessing properties of slag-cement using a comparison of the compressive strengths at 28 days of mortars as follows:

$$\text{Hydraulic Index } \left(\frac{70}{30}\right) = \frac{a-c}{b-c} \times 100 \qquad (2\text{-}7)$$

where a = the strength developed in the mortars of portland slag cement;

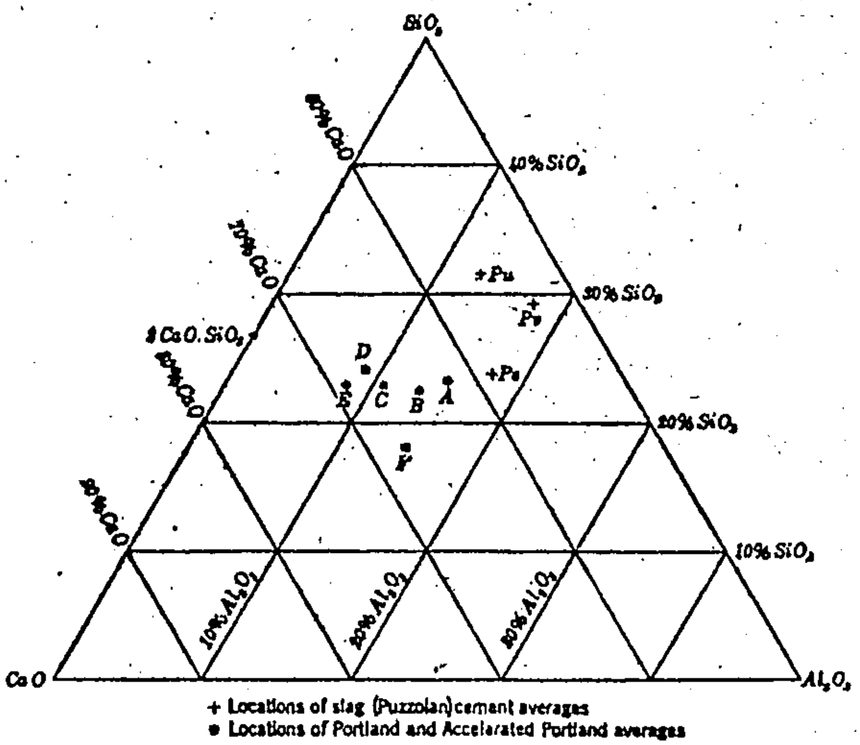
b = the strength developed in portland cement mortars alone;

c = the strength developed in the portland cement and ground quartz sand (sand ground to a Blaine of 4000 (cm^2/gr) cement mortars); and,

70/30 indicates that the portland cement by weight of total cement is 30%.

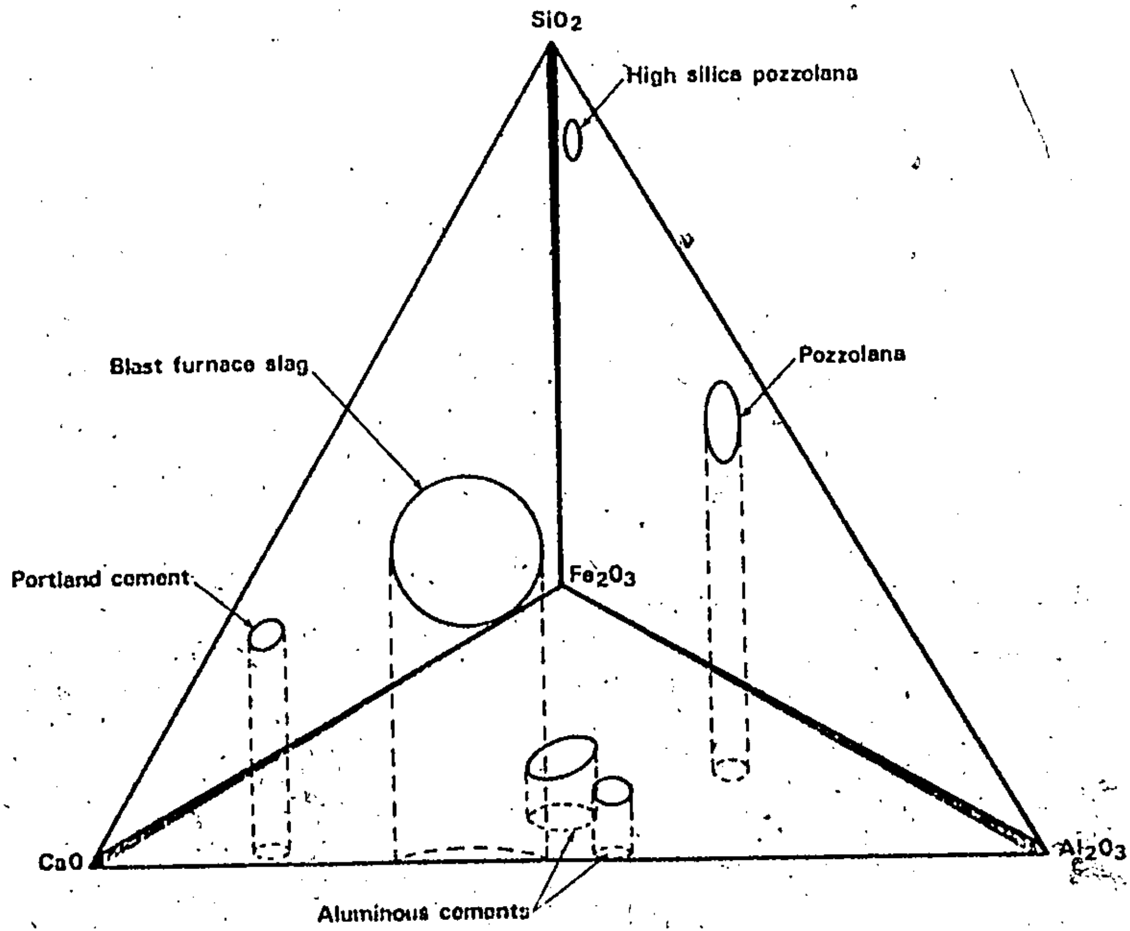
This index does not include the chemical composition and is found to vary with the proportion of slag present in the cement, say 50/50, 30/70, etc.

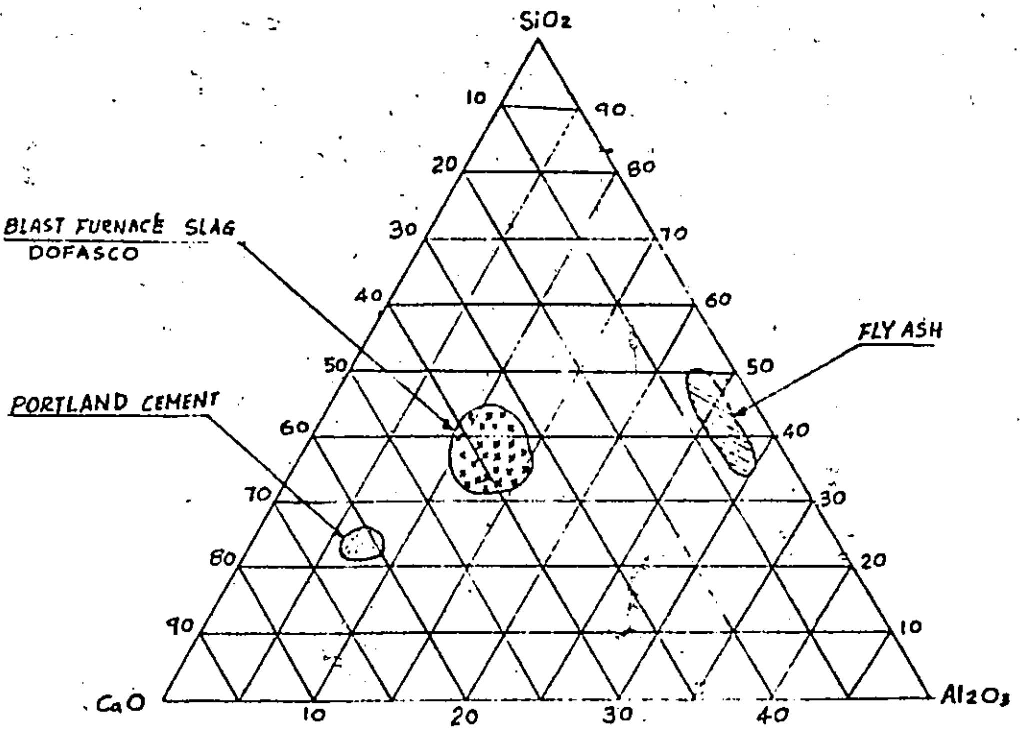
FIGURE 2-14
TERNARY AND TETRAHEDRON
DIAGRAM



Composition Fields of Old and Modern Portlands and of Slag Cements.

(a) [22]




SiO2
10
20
30
40
50
60
70
80
90
90
80
70
60
50
40
30
20
10
CaO
10
20
30
40
Al2O3
BLAST FURNACE SLAG
DOFASCO
PORTLAND CEMENT
FLY ASH

(c)

Mortars of low water-cement ratio (w/c = 0.32) must not be used for the test.

The fineness of the ground slag influences the cementing properties and cementing rate as indicated by typical data in Table 2-35. This effect is not a direct property of slags themselves, but does depend on the chemical composition and granulation process to the extent that these affect the grindability of the slags. The fineness contributes to the cementing properties and rate by providing more surface for the reaction [76]. It is known that, other factors being equal, the chemical activity of a substance is directly proportional to the surface per unit weight (specific surface). Theoretically, there is no limitation on the fineness of cementing materials, but there are economic and technical limits. Although the object of grinding slag is to facilitate chemical reactions between the slag and water, there are some practical considerations that must be taken into account. For example, if the particles of the ground slag are too small, some hydration may occur in the package during storage, and the control of set may become difficult, largely obviating the high grinding costs.

Manufacture

Unlike the manufacture of portland cement which is started with the preparation of raw materials and involves clinkering and then final grinding; grinding is the only process in slag cement manufacture except for a minor initial drying process which is completely omitted in the wet process, referred to as "cold process" cement [18, 43].

ASTM C595-72, the standard specification for blended hydraulic cements requires the slag cement to have a Blaine fineness of 4700 cm^2/gr

TABLE 2-35

EFFECTS OF SLAG (a) FINENESS ON STRENGTH OF CONCRETE [43]

FINENESS (b)	COMPRESSIVE STRENGTH (psi) (c)				
	1 Day	3 Days	7 Days	28 Days	90 Days
3095	104	360	855	2460	3950
3930	127	417	1220	3160	4690
4850	152	522	1535	3600	5270
6140	173	707	1810	3925	5670
100% Portland Cement	915	2415	3510	4950	6370

(a) Hydraulic modulus = 1.0

(b) By air permeability cm^2/gr

(c) 30:70 portland cement: slag in 1:2:4 (vol) gravel concrete, w/c = 0.55, water stored (by the air-permeability method), being much higher than the usual portland cement requirement of 2800 cm^2/gr. The Cemsave Cement Company specifies the fineness of their slag cement to be not less than 3250 cm^2/gr [93]. As the slag must be ground to extreme fineness, it is necessary that moisture due to water cooling for granulation or pelletizing be reduced as much as possible, to about 0.25% or less.

The temperature utilized in drying must not be high enough to start re-fusion of the slag. However, drying at elevated temperatures below that for re-fusion is desirable as it will result in materially acceleration the set of the resulting cement and also in increasing the strength of specimens made from it [22]. In the dry grinding method, as in the case of portland cement manufacture, various types of driers, such as rotary, non-rotary by gravity, and tandem driers are used. The rotary drier is the most common in use. Dried materials then move into the grinding mill which is usually of the tube type. In order to regulate the set of the slag cement (usually to accelerate the set), special additives are introduced before, or during, the grinding process. The Whiting process, patented in the U.S. in 1895, covers the use of caustic soda, potash, sodium chloride, or equivalents as aqueous solutions or in a dry state at any stage of the manufacturing process [18, 22]. Another example of additives is the use of up to 1% sodium sulphate or gypsum [43] in supersulphate cement [47].

The dry process of slag cement manufacture is most often used, but some plants utilize the wet process avoiding the necessity of drying the slag. In the wet process, a slurry containing a ground high-lime slag will have a definite tendency to thicken and gradually set into a cake due to the latent cementitious properties of the granulated slag. This trouble has been controlled by the addition of a small amount of sugar which delays the set of the slurry [43].

Instead of using commercial mill processes, in some instances slag cement has been ground and blended with other materials on the site of the construction project, or in the concrete unit products plant. These operations can be carried out both by the dry-grinding method used in the ordinary plants, and by a wet process such as the Trief process. The Trief wet grinding process [18, 43] developed by V. Trief in Belgium was applied to the Bort dam construction which is a gravity arch structure involving over 860,000 cubic yards of concrete. Slag was shipped to the site and ground there to a slurry and blended with portland cement and minor proportions of sodium hydroxide ($NaOH$) and common salt ($NaC\ell$). The final blend consisted of:

Granulated slag	68.65	(15-40% water content);
Portland cement	30.00%	and,
Common salt	1.35%	(accelerator).

This Trief wet process made drying of the slag unnecessary, and high efficiency was obtained in grinding to high fineness. The Trief process has been used in the manufacture of concrete products in Belgium, and other dam construction such as the Cluanie and Aron dams in the U.K. [43].

Aging effects on the cementing properties of slag cement have not received much attention. However, this does not mean that there is no age problem with slag cements. Lea [43] studied slag's sensitivity to deterioration in storage and its low strength in comparison with modern portland cements, and indicated that this is one of the reasons for the abandonment of slag-cement production in many countries.

Hydration of granulated slag with or without adding various activators

The process of the hydration of ground slag alone, and with the addition of activators such as lime (for slag cement), portland cement (for portland blast furnace slag cement) and calcium sulphate (for super-sulphate cement), and the final products involved in the set by hydration are hard to define and may not be unique. These hydraulic reactions are dependent upon the proportion of the slag fines and activator, compaction energy, aggregates utilized, curing methods (temperature and duration) and humidity. Even in the same sample, various methods of analysis and their accuracy may lead to different results and conclusions. To simplify the interpretation of test results, the combinations tested usually involve only one or two variables while the others are held constant for the specific conditions.

Most experiments have been done with the intention of getting the variational mode and comparison. For example, the comparison of strength between mixes using different aggregates may be misleading, however the comparison of mixes with differing lime ratios and time of processing for any one of the aggregates will provide useful data. It is very difficult to find experimental information on the hydration of slag fines without any activators. This is because it has been considered that the reaction is too weak to detect and it is not practical to obtain definite results.

The mineralogical composition is quite different for granulated slag and portland cement, however the chemical composition of both is very similar except that the lime content of slag is lower than that of portland cement. This is indicated in Table 2-21. This gives an indication that the hydration products of slag cement are probably similar to those of ordinary portland cement. As in the portland cement hydration in which $Ca(OH)_2$ is released, the slag hydration is closely related to the amount of lime in the complicated reaction system. The effect of the lime has been explained [32] in that the hydration is due to a gel coating on the surfaces of slag particles and appropriate activators can either react with these films or release enough $Ca(OH)_2$ to break these films. Portland cement provides $Ca(OH)_2$ [43] by the reaction itself:

$$2(3CaO \cdot SiO_2) + 6H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2;$$

and, $2(2CaO \cdot SiO_2) + 4H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$ [55]

When ground granulated (or pelletized) slag is placed in water, or a specimen mixed with water is cured in a water bath, slag fines on the surface in direct contact with the water cannot harden. Lea indicates [43] that this is due to the formation of an acidic surface film as a small amount of Ca^{++} ions are released into the solution. The deficit amount of Ca^{++} ions, which open up the silicate framework of the glass so as to accelerate the rate of hydration, can be supplied by activators. Thus a lime activator prevents the formation of an impermeable alumino-silicate film and progressively combines with the slag. In the case of sulphate activators, the initial reaction is the formation of calcium sulpho-aluminate due to attack on the alumina, and this must be considered to break up the silicate structure. However, if excess lime is utilized and the curing time is long, dicalcuim silicate alpha-hydrate is formed at the expense of the tobermorite gel which is the main source of strength gain as in the case of ordinary portland cement.

A very low amount of added lime may not be adequate for full hydration of the slag. Consequently, there will exist an optimum level of lime cement to be made up from residual lime and added lime activator. Midgley and others have made tests [51] on the reaction between lime and granulated slag (41.5% CaO, 33.75% SiO_2, 0.51% Fe_2O_3, 15.84% Al_2O_3 and other minor compounds) to find out the optimum lime content. One of the test results (using X-ray diffraction methods) indicated that free lime was always present in the mixes after autoclaving, except in the case of 10:90 (lime:slag) mix after at least six hours autoclaving. The quantity of free lime detected increased as the percentage of lime in the original mix increased; the maximum quantity of lime which the slag required to react was about 10%. The X-ray diffraction data for some of the mixes of lime and slag are shown in Table 2-36. From Table 2-36, for slag alone (100% slag) the hydrate phases are poorly crystallized tobermorite gel and hydrogarnet. At 5% lime addition, more tobermorite and hydrogarnet are formed for the same curing time with a trace of dicalcium silicate α-hydrate.

Another test series involved compressive strength tests with the same fine slag and added lime of 0.5% up to 40% by weight of the slag. The autoclave curing period is also varied. The results, as shown in Table 2-37 and Figure 2-15, indicate that a mix of 5% added lime gives the highest strength (optimum lime content) at sixteen hours curing.

On the other hand, Gutt estimates the optimum amount of lime to be

TABLE 2-36

X-RAY POWDER DIFFRACTION DATA FOR THE MIXES OF LIME AND SLAG [51]

100% slag 16 h at 160 lb/in²			C88 5% lime, 95% slag 16 h at 160 lb/in²			C23 10% lime, 90% slag 6 h at 160 lb/in²			C80 10% lime, 90% slag 48 h at 160 lb/in²			C35 40% lime, 60% slag 2 h at 160 lb/in²		
d(Å)	I/I₀	Identification	d(Å)	I/I₀	Identification	d(Å)	I/I₀	Identification	d(Å)	I/I₀	Identification	d(Å)	I/I₀	Identification
			5·44	m	T, α									
			4·98	ms	H	4·96	vw	CH	4·98	mw	H, CH	4·34	vvw	H
			4·33	m	H				4·22	vvw		4·20	vw	α
												3·90	w	α
			3·565	vvw	α	3·68	vw	α				3·68	w	α
			3·27	m	α	3·25	m	α	3·25	s	α	3·50	vvw	α
3·04		T	3·05	vs	T	3·04	vs	T	3·04	vs	T	3·25	s	α
2·71	m	H	2·72	vvs	H	2·72	vs	H	2·72	vs	H	3·07	s	T
			2·59	vw	H	2·62	w	CH	2·58	vvw	H	2·74	s	H
			2·48	ms	H	2·49	w	H	2·49	w	H	2·62	vvs	CH
2·29	m		2·29	ms	H+slag	2·41	vvw	α	2·395	mw	α	2·51	mw	H
			2·22	s	H	2·22	m	H	2·22	m	H	2·40	ms	α
			2·03	mw	H	2·03	w	H				2·23	m	H
1·97	m	H	1·97		H	1·97	m	H	1·97	ms	H	2·15	vvw	α
			1·92	w	H	1·92	w	H	1·925	w	H	1·99	vvw	H
			1·83	w	T	1·835	vw	T	1·83	vvw	T			
1·75	m		1·75	s	H+slag	1·745	vw	H+slag	1·78	vvw	H+slag	1·785	w	H+slag
			1·72	vvw	H									
			1·68	m	H, T	1·685	m	H, T	1·68	m	H, T	1·70	w	H, T
1·62	m	H	1·62	s	H	1·625	m	H	1·62	m	H	1·64	m	H
slag + a hydrogarnet + tobermorite			slag + a hydrogarnet 3 $CaO.Al_2O_3.SiO_2.2H_2O$ + tobermorite + dicalcium silicate alpha-hydrate			slag + a smaller amount of hydrogarnet than C88 + tobermorite + dicalcium silicate alpha-hydrate + trace of $Ca(OH)_2$			slag + hydrogarnet as C23 + tobermorite + dicalcium silicate alpha-hydrate			slag + a smaller amount of hydrogarnet than C23 + tobermorite + dicalcium silicate alpha-hydrate + a lot of $Ca(OH)_2$		

T = tobermorite. CH = calcium hydroxide. H = hydrogarnet phase. α = dicalcium silicate alpha-hydrate.

TABLE 2-37

COMPRESSIVE STRENGTHS OF CYLINDERS (psi) [51]

ADDED LIME PERCENT	SLAG PERCENT	PERIOD OF CURING (HOURS)			
		2	6	16	48
0	100.0	...	177	3780	...
0.5	99.5	...	2460	...	...
1.0	99.0	...	3410	...	...
2.5	97.5	...	...	6650	...
5.0	95.0	...	5272	8589	...
10.0	90.0	4114	4017	4639	6910
20.0	80.0	2337	3652	3628	3342
30.0	70.0	1887	2811	3600	3165
40.0	60.0	1546	2114	2434	2951

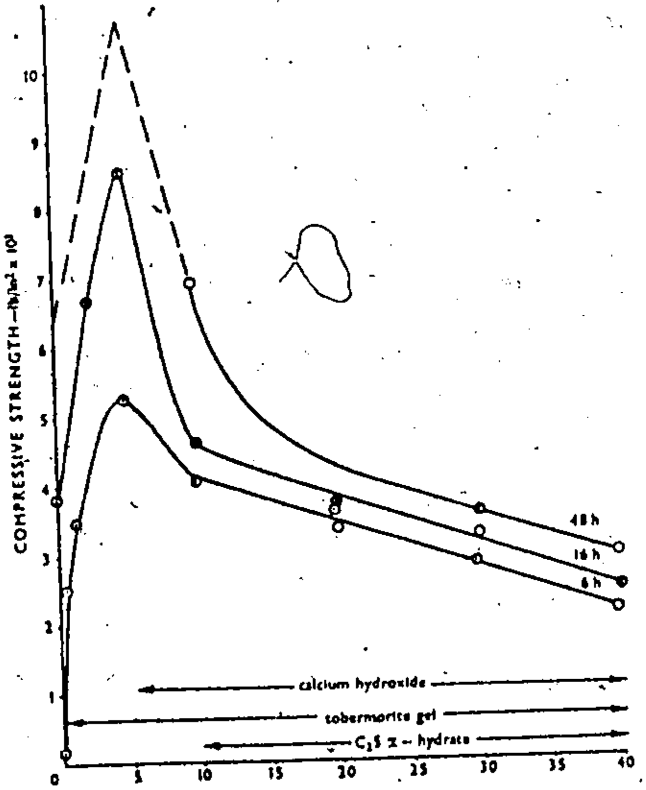


FIGURE 2-15 RELATION BETWEEN COMPRESSIVE STRENGTH AND PERCENTAGE OF LIME ADDED FOR VARIOUS PERIODS OF AUTOCLAVING [51]

approximately 15% in slag [32], a much higher figure. Lea determined the residual calcium hydroxide present in cured slag cement [43]. The amount of $Ca(OH)_2$ varied with the portland cement to slag ratio in the cement. For the lower percentage of portland cement $Ca(OH)_2$ may not be detected in the later stage of hydration. Figure 2-16 shows these test results. Lea assumed that optimum results require a total of about 10% high-calcium lime with the normal granulated slag of high lime content. Many investigators have examined the final products resulting from the hydration. Each case involved a different combination system from the others. In the slag + lime [51] and slag + portland cement [32, 43, 47] combinations, the most common products found are Tobermorite, Ellringite, Hexagonal Calcium Aluminate Hydrate, Tricalcium Aluminate Mono-sulphate Hydrate and Calcium Hydrate.

Usually, in the well cured condition, a green colour can be seen in a portion of the test specimens. This colour comes from the polysulphides ($3CaO\ A\ell_2O_3\ .\ S.\ N\ H_2O$) which are formed with sulphur in the presence of $Ca(OH)_2$, emitting the odour of hydrogen sulphide (H_2S) [18, 22, 43, 47]. If the specimen has been exposed to salt water, this colour is more clear [22]. But when the specimen surface is exposed to dry air, the green colour will turn white and disintegrate due to the oxidation of its sulphides [18].

The specifications for the cements related to granulated slag are summarized in Table 2-38, which is helpful in understanding the influencing factors for practical application purposes.

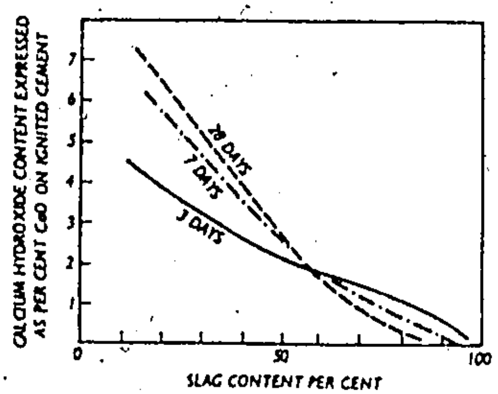


FIGURE 2-16 CALCIUM HYDROXIDE CONTENT OF SET BLAST FURNACE CEMENTS [43]

TABLE 2-38

SPECIFICATION OF CEMENT RELATED TO SLAG

COUNTRIES	SLAG CEMENT (ACTIVATED BY LIME)	PORTLAND-BLAST FURNACE SLAG CEMENT (ACTIVATED BY PORTLAND CEMENT)	SUPERSULPHATE CEMENT (ACTIVATED BY CALCIUM SULPHATE)
Belgium	NBN 49 Ciment de laitier Strength requirement Normal - LN Special - LS Special - LS 400 not less than 75% of granulated slag	...	NBN 132 Ciment métallurgique sursulfaté
France	P15-306 Designition CLX 160 not less than 70% of granulated slag SO_3 max 5%	Ciment de fer 25-35% Ciment métallurgique mixte 45-75% Ciment de haut fourneau 65-75% Ciment de laitier au clinker +80% } slag	NORME P15-313 Ciment sursulfaté
Germany	...	DIN 1164 (1967) Eisenportland cement - not less than 40% Hochofen cement - 41-85% } slag $\frac{CaO+MgO+A\ell_2O_3}{SiO_2} \geq 1.0$ SO_3 max 3.5% (Eisen), 4-4.5% (Hochofen)	DIN 4210 Sulfathütten zement
U.K.	...	BS 146-1958 not less than 65% of slag	BS 4248 (1968)
U.S.	ASTM C595-72 slag cement S type, SA type SO_3 max 4% S max 2% not less than 60% of slag	ASTM C595-72 portland blast furnace slag cement IS SO_3 max 3% S max 2% 25-65% of slag	...

2-3-3 Pozzolanic Reaction

Pozzolans which as indicated previously are not cementitious in themselves, contain constituents which will combine with lime at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementing properties. Pozzolans can be classified into two main groups; natural pozzolans and artificial pozzolans. The materials of volcanic origin (volcanic ash deposits), diatomaceous earths, and diatomite of opal belong to the natural group. Volcanic ash, which contains highly crystalline materials is much more stable and thus shows low pozzolanic activity. The weak pozzolanic activity that is present is due to the volcanic glass and altered zeolite compounds formed by the action of superheated steam and carbon dioxide below the earth's surface. Pumicites and zeolite are also classified in this family.

Heat-treated or burnt clays, oil shale, ground brick, ground siliceous rocks and fly ashes belong to the artificial group which is mainly derived from industrial wastes. Burnt clays have been used in the past in mortar and concrete, mainly when portland cement was not available. Pozzolanic cement consisting of ground burnt clay and portland cement was described in 1909 by Potter [43].

The value of the pozzolans as a cementing material is due to the reaction between the siliceous compounds and added lime, which is dependent on the glass content, chemical or mineralogical composition, fineness [39, 43] and many other factors. In considering the importance of the glass portion of pozzolans, Majumdar [47] classified them as volcanic glasses, zeolitized glasses and finely divided amorphous silica. Many attempts have been made to explain the mechanism by which lime and a pozzolan react to form cementitious compounds, but no definite explanation of the mechanism has been established. Lea [43] has indicated that the two main theories used to explain the lime-pozzolan reaction are a base exchange process and a direct combination process. Base exchange theory was indicated by zeolite compounds acting as natural pozzolans owing their properties to base exchange. According to later studies, it was found that the major reaction was not actually base exchange, but the formation of new hydrated compounds. This direct combination to form new hydrated compounds can be followed by the Florentin method which is based on the insolubility of pozzolans in cold hydrochloride acid and their solubility in the same reagent as the lime-pozzolan reaction products [43].

Pozzolanic reaction processes have been investigated [22, 51] using the lime-aggregate ratio, autoclaving period, or combinations, with an X-ray analysis of the resulting products. One of these studies [51] has been done using fly ash (main components : 42.9% SiO_2; 26.70% $A\ell_2O_3$; 7.90% Fe_2O_3; and 4.10% CaO) and commercial hydrated lime of 73.52% CaO. From the test results, it may be inferred that an increase in the lime-aggregate ratio or the autoclaving period materially helps in the development of the crystalline perfection of the tobermorite. According to tests on a 40:60 (lime: fly ash) mix, it can be assumed that during the longer steam treatment new tobermorite is being formed in the gel state, while already existing gel is crystallized, so that there is always about the same qualitity of poorly crystallized tobermorite gel. As the lime-silica ratio is increased, or the autoclaving time is extended, the gel crystallizes and some hydrogarnet is also formed [51].

Another test [39] indicates that the gel-like material which comes from the reaction of lime and fly ash becomes sufficiently crystalline after about one week to be identified by X-ray analysis. After eight weeks curing, calcium silicate hydrate of the tobermorite groups can be identified. At this stage the reaction products have coated reactable ash particles, and any further reaction that may occur is due to further available $Ca(OH)_2$ breaking through this formed coating around the particles. The rate of strength development decreases since the pozzolanic reaction is now largely controlled by the breakthrough and diffusion actions.

There are numerous methods available for evaluating pozzolanic activity. The various methods are summarized in Table 2-39. Among them, the most direct and reliable method for practical purposes is a strength development test, but this method is relatively time consuming and costly. The analytical methods are indirect but must be verified and correlated with actual performance. Difficulty may still exist in interpretation of experimental results using various analytical techniques and performance tests since the pozzolanic activity is influenced by so many factors: glass content, chemical composition, fineness of pozzolans and chemical composition of limes.

Ahlberg and Barenberg [2] studied the solubility of both the crystalline (or quartz) and amorphous forms of silica in water. The resulting higher solubility of the amorphous form over the crystalline is shown in

TABLE 2-39

EVALUATION METHODS FOR POZZOLANS

GENERAL EVALUATION	METHOD	EVALUATION[a]
Physical	General grain shape	Related to workability.
	Particle size distribution	Related to fineness, glass content for F.A.
	Specific gravity	Weight of mixture.
	Fineness	Strength development. Air permeability method. Nitrogen adsorption method [15].
Analytical	Chemical analysis	Yield oxide content from which potential compounds can be computed.
	Petrographic analysis	Identification of active minerals present.
	X-ray Diffraction analysis	Identify crystalline substances.
	Differential Thermal analysis	Supply information about amorphous substance present.
	Electronic Microscopic analysis	Glass formation and contents.
	Solubility test	NaOH solution.
	Lime Absorption test	Place the powdered pozzolan in a saturated lime solution.
Performance	Strength test	Vary with aggregate used and many other factors. Most reliable method.
	Set test	Initial or final set for paste.
	Insoluble resistance test	Activity test of pozzolan and lime paste.
	Uncombined lime test [10,43]	Reactivity test pozzolan-lime paste.
	Resistance to leaching, sulphate attack test	...
	Reduction in alkali-aggregate expansion and dry shrinkage	...

Figure 2-17. From this test, it would appear that only the amorphous form of silica can enter into the pozzolanic reaction. However, when considering the silica-lime-water system, the effect of the lime on the PH of the solution with temperature must be taken into account. Lime releases less Ca^{++} ions in a $Ca(OH)_2$ solution at higher temperatures as indicated in the section on lime properties. There may exist a temperature which optimizes the conditions for the maximum solubility of lime and amorphous silica. The solubility of amorphous silica increases rapidly with increasing alkalinity and logically seems to be affected by particle size and the interfacial surface energy of the silica.

X-ray diffraction studies [52] indicate that most crystalline materials present in fly ashes do not enter into the reaction at ambient temperatures, but amorphous compounds of silica, alumina, and iron oxide in the fly ash are involved in the reaction. The use of X-ray diffraction methods is not a convenient means of identifying the reactive constituents of fly ash because these constituents are apparently restricted to the non-crystalline glassy materials that are not detectable with diffraction methods. The degree of crystallinity, i.e., the amount of glassy phase, influenced the pozzolanic activity to a much greater degree than did fly ash particle size within the curing period of eight weeks as shown in Figure 2-18 [39]. A detailed description of the synthetic fly ashes used in this test are shown in Table 2-40 and other details are: Mixes - 1:2 (lime: fly ash) proportions; distilled water used to optimum moisture content; specimens 1 inch in height, half-inch in diameter; cured at 23±2°C; and, analytical reagent grade lime utilized throughout. Chemisorption of calcium ions released from the lime on the

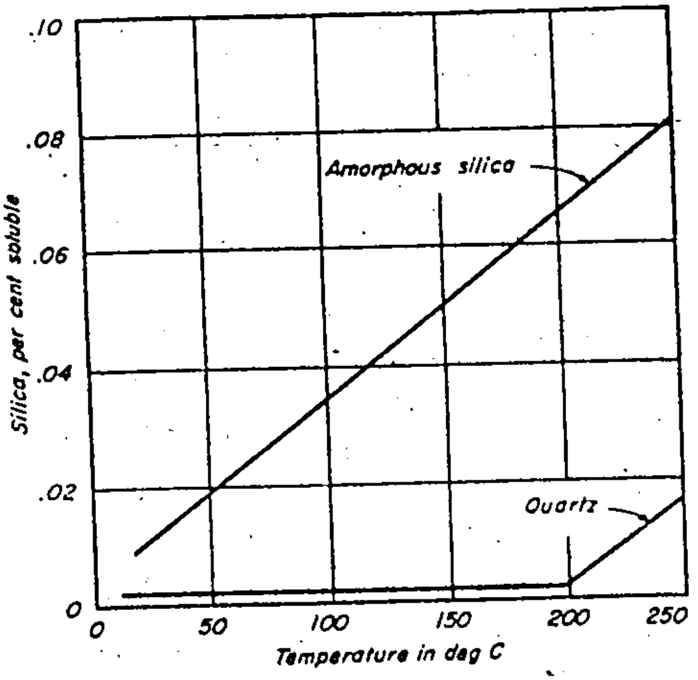


FIGURE 2-17 SOLUBILITY OF SILICA IN WATER
AS AFFECTED BY TEMPERATURE [2]

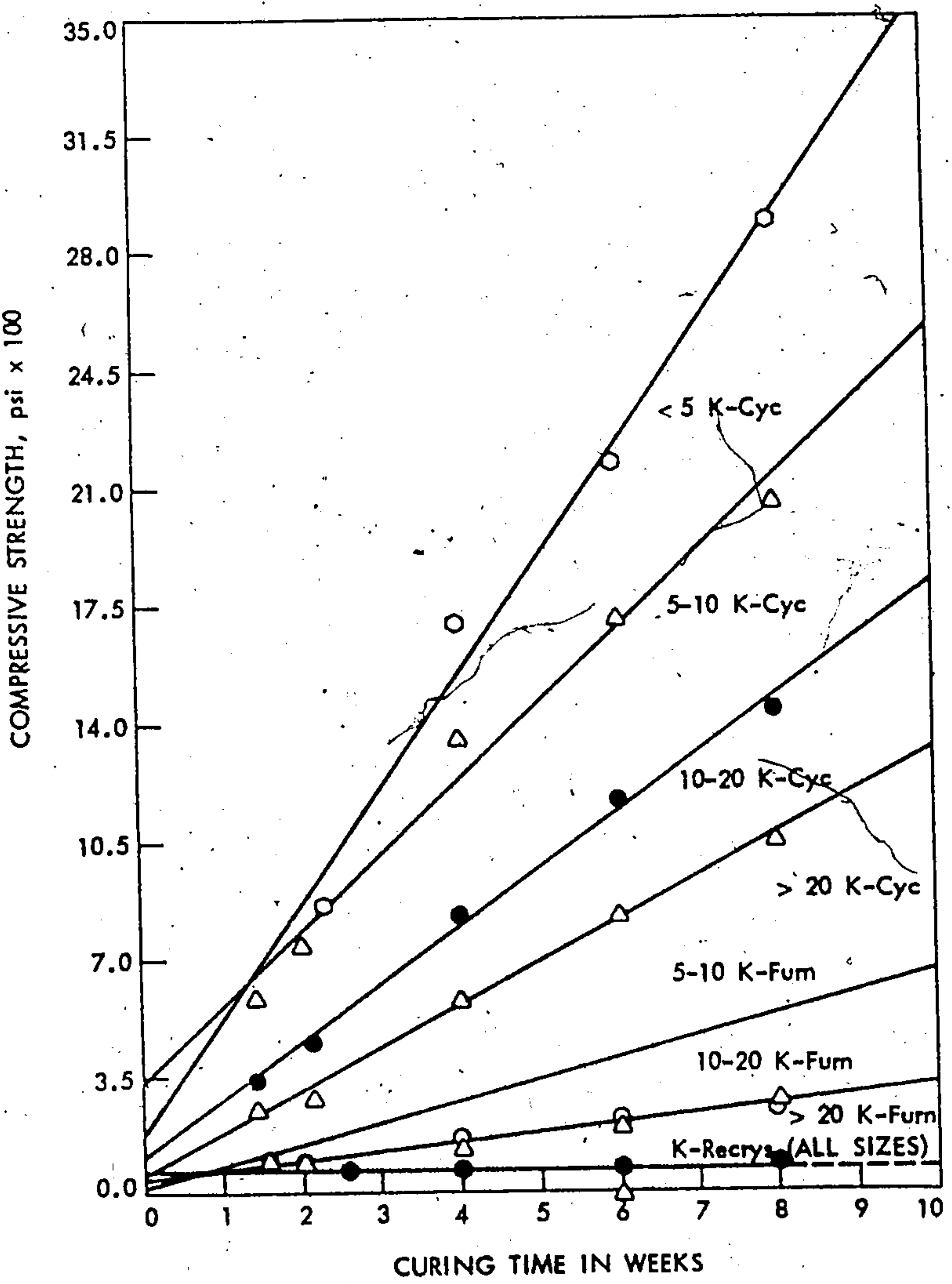


FIGURE 2-18 COMPRESSIVE STRENGTH FOR VARIOUS TYPES OF FLY ASH WITH LIME [39]

glass content - K-Cyc most amorphous fly ash
K-Furn intermediate " "
K-Recrys least " "
mix proportion 1:2 (lime: fly ash)

TABLE 2-40

PROPERTIES OF SYNTHETIC FLY ASHES

MATERIAL CODE	PARTICLE SIZE	GLASS CONTENT	DESCRIPTION
5K-Cyc	<5 µm	most amorphous	Kaolinite ash collected in cyclone separator
5-10K-Cyc	5-10 µm		
10-20K-Cyc	10-20 µm		
>20K-Cyc	>20 µm		
5-10K-Furn	5-10 µm	intermediate	Kaolinite ash deposited in furnace
10-20K-Furn	10-20 µm		
>20K-Furn	>20 µm		
K-Recry (all sizes)	all sizes	least	K-Cyc ash soaked at 1500°C and slowly cooled

75 µm is equivalent to #200 sieve

surface of silica and crystalline portions are complementing factors in the pozzolanic reaction [2].

The compressive strength and tensile strength tests for pozzolanic reaction using mortar specimens are most commonly used, and the strength development in lime-pozzolan mortars is found to depend on: the ratio of lime to pozzolan in the mix; type of lime and pozzolan; and, type of soil and/or aggregates associated with the mix. In order to investigate the optimum lime content, the estimation of the amount of uncombined lime in the set lime-pozzolan mixes or pozzolan-cement has been done using various methods such as: Franke method; Calorimetric method; differential thermal analysis (D.T.A.); and, extraction with partially saturated $Ca(OH)_2$ solutions. The maximum amount of lime that is taken up at an age of one year is about 50 grams per 100 grams pozzolan in 1:1 (by weight) hydrated lime-pozzolan mixes [43].

Minnick indicates that [52]: a lime-pozzolan ratio of 1:10, which is very low, may be the optimum for some lime-fly ash-aggregate mixtures; marked increases in compressive strength were generally obtained with increases in the lime to fly ash ratio up to 1:3 by weight; only slight additional increases were obtained with high lime to fly ash ratios of up to 1:1.5. For both granular and clayey soils 5 % to 9% lime and 10% to 25% fly ash by weight of total mix are typical proportions, giving lime-fly ash ratios of about 1:2. The POZ-O-PAC Company of America have used 2.5 % to 4% lime and 10% to 15% fly ash by weight of total mixes for slag aggregate stabilization. Typical strength development and proportions for this type of material are shown in Table 2-41.

TABLE 2-41

STRENGTH OF LIME-FLY ASH-AGGREGATE MIXES
(After General POZ-O-PAC Co. [103])

MIX NO.	UNIT	1	2	3	4	5	6	7	8′	9	10
Lime	%	2.5	3.0	4.0	2.8	4.0	4.0	3.0	3.5	3.0	4.0
Fly ash	%	11.0	12.5	12.5	14.1	12.5	12.5	15.0	10.0	12.5	12.5
OH slag (aged)	%	86.5	84.5	...	...	...	...	...	...	...	...
OH slag	%	...	...	...	...	...	...	...	86.5	84.5	83.5
Air-cooled slag	%	...	...	83.5	...	...	...	...	...	...	...
40% air-cooled slag 60% OH slag	%	...	...	...	83.1	83.5	83.5	82.0	...	...	...
Water content	%	7.0	7.0	6.5	...	6.0	6.5	6.5	7.7	6.8	7.5
Curing age	day	...	...	7	...	7	7	7	7	7	7
Curing temp.	°F	...	...	100	...	100	100	100	100	100	100
Strength	psi	805	775	570	...	1095	870	1000	1470	1110	1420
Dry density	pcf	157.9	151.6	124.3	143.1	151.6	151.3	145.7	160.7	154.9	157.8

The curing period affects the optimum level of lime consumption. The strength developed in the lime-pozzolan mortars as shown in Table 2-42 indicates that at an early age the maximum strength is obtained with a lime-pozzolan ratio of about 1:4 with finely ground materials, but at a longer age, the optimum ratio moves towards mixes of higher lime content and approaches about 1:3 to 1:2 at over one year [42].

When dolomite limes ($Ca(OH)_2 \cdot MgO$, $Ca(OH)_2 \cdot Mg(OH)_2$) rather than high calcuim hydrated lime are used in pozolanic reactions, the role of magnesium oxide, which is a major component of the dolomite limes, is important. This has been studied by Minnick [52]. Minnick indicates that the magnesium oxide which is present in the dolomite limes used in the study will hydrate over an extended period of time, and the amount of magnesium oxide present in the lime-fly ash specimens decreases with time with a disproportionately small increase in magnesium hydroxide. It is possible that the simultaneous reactions:

$$MgO + H_2O \rightarrow Mg(OH)_2 \text{ ; and}$$

$$Mg(OH)_2 + SiO_2 + H_2O \rightarrow X\ MgO.Y\ SiO_2.Z\ H_2O$$

are occuring, resulting in a poorly crystallized reaction product similar to that obtained from the calcium ions. Since magnesium oxide is lower in molecular weight (40.3) than calcium hydroxide (74), more unit reaction can occur per equal weight of magnesium oxide, thus resulting in more potential cementitious products. Based on these considerations, the lime types can be ranked chemically in decreasing order of their pozzolanic receptivity as follows:

1. Dolomitic monohydrated lime $Ca(OH)_2 \cdot MgO$

TABLE 2-42

EFFECT OF POZZOLAN TO LIME RATIO ON STRENGTH WITH AGE OF MORTARS [43]

POZZOLAN	MIX PROPORTIONS BY WT.			TENSILE STRENGTH (psi)			
	HYDRATED LIME	POZZOLAN	STANDARD SAND	7 DAYS	28 DAYS	90 DAYS	1 YEAR
Burnt Shale	1	1	6	107	207	341	521
	1	2	9	133	322	459	560
	1	4	15	203	371	514	533
Trass	1	1	6	213	361	447	477
	1	2	9	225	390	425	495
	1	4	15	234	363	412	433

2. High calcium hydrated lime $Ca(OH)_2$
3. Dolomitic dehydrated lime $Ca(OH)_2 \cdot Mg(OH)_2$

This ranking is supported by the test results for strength using various limes in lime-fly ash-aggregate mixes (5% lime, 20% fly ash, 75% graded Ottawa sand by weight) with a preparation moisture content of 8%, cured seven days at 38°C, and tested according to ASTM C593-69 as shown in Table 2-43.

It is generally accepted that the pozzolanic activity will increase with an increase in specific surface and decrease with an increase in carbon content (if any is present) of the pozzolanic material provided that all the other conditions remain constant. Typical test results [39] showing the effect of specific surface or fineness on the strength and rate of strength gain ~~are~~ shown in Figures 2-19 and 2-20, respectively. The finer fraction of the same fly ash shows a higher strength development than the coarser fraction in Figure 2-20. This higher strength can be attributed to two causes: the finer fraction material has a higher specific surface available for reactions; and, the finer particles generally include the higher glass contents according to studies on particle size distribution and glass content [46].

Gabrera and Gray [15] have recently studied the specific surface of fly ash from various sources as related to carbon content, total silica and alumina content, and pozzolanic activity. The surface area was determined by various methods such as air-permeability (Blaine), nitrogen-adsorption, glycerol retention, and iodine adsorption. Specific surface was also calculated from the particle size distribution of the fly ash. It was found that each method gives very different

TABLE 2-43

LIME TYPE EFFECT ON STRENGTH [52]

TYPE OF LIME	CHEMICAL ANALYSIS (%)								STRENGTH (psi)
	CaO	MgO	CO_2	SiO_2	Fe_2O_3	$A\ell_2O_3$	H_2O	LOSS ON IGNITION	
Commercial High Calcium Hydrate	72.6	0.7	3.4	0.8	0.2	0.0	1.0	26.1	780
Carbide By-product High Calcium Hydrate	70.3	0.2	1.1	1.7	0.4	1.1	4.8	24.5	180
Commercial Monohydrated Dolomitic Lime	47.1	33.8	3.4	0.6	1.1	0.1	0.9	17.9	1160
Commercial Monohydrated Dolomitic Lime	46.0	31.2	1.2	1.4	...	...	1.0	19.3	920
Commercial Dihydrated Dolomitic Lime	42.3	30.1	3.4	0.6	0.5	1.0	0.5	25.5	770

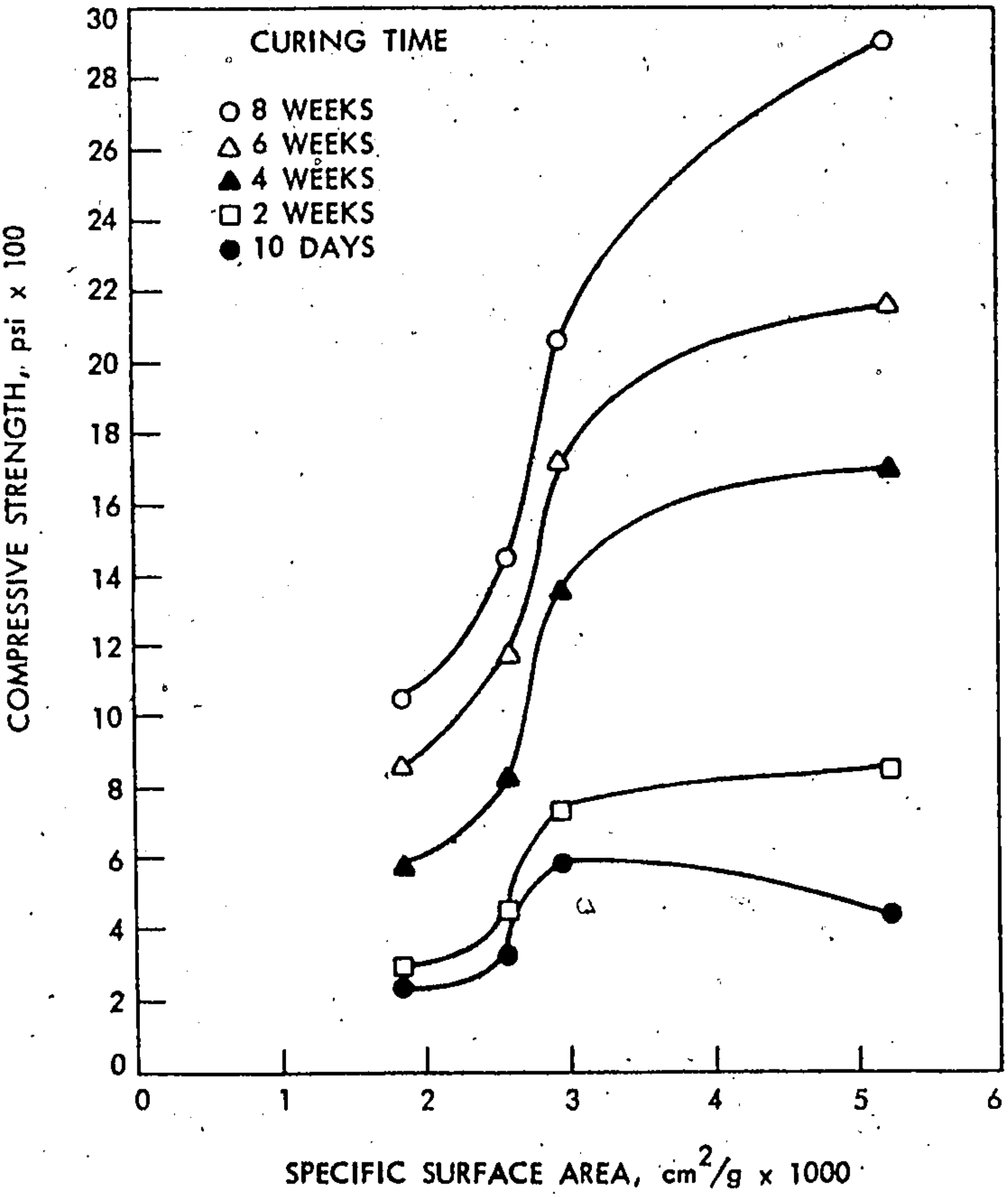


FIGURE 2-19 COMPRESSIVE STRENGTH vs SPECIFIC SURFACE AREA OF FLY ASH [39]

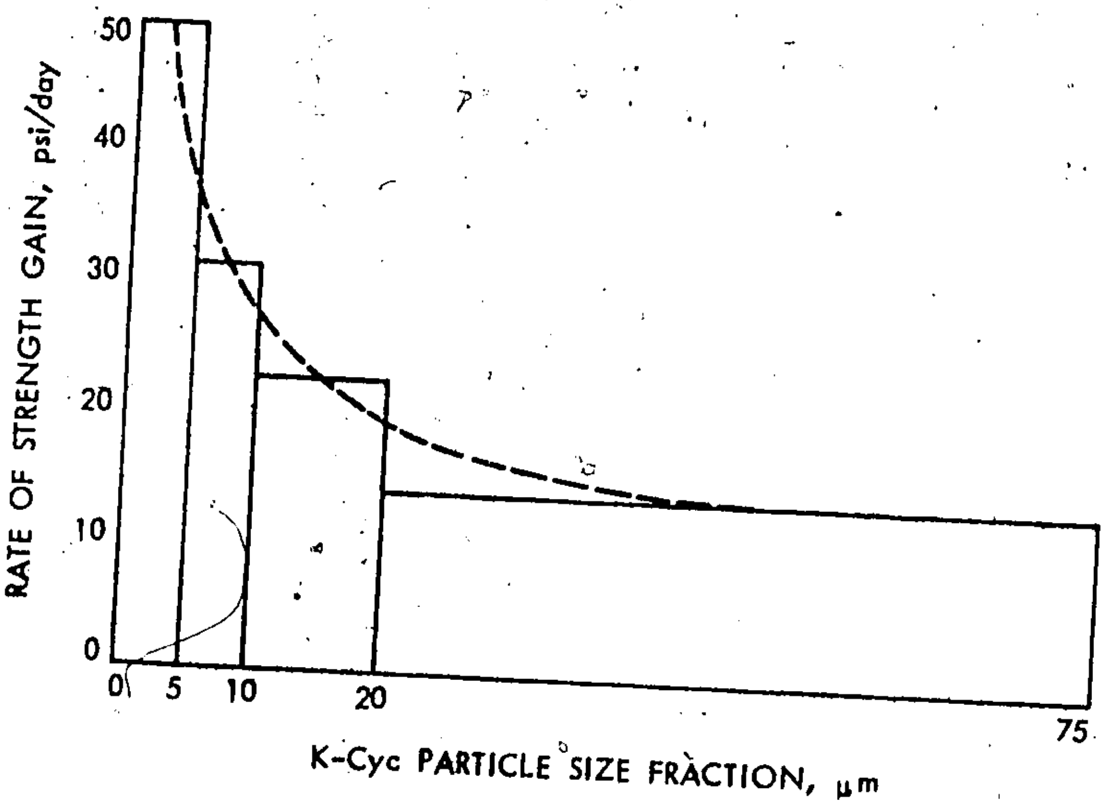


FIGURE 2-20 PARTICLE SIZE FRACTION OF FLY ASH vs RATE OF STRENGTH GAIN [39]

values of specific surface as shown in Table 2-44.

The different values of specific surface determined by the nitrogen adsorption and air-permeability methods on a particular ash are actually based on a different concept of the effective surface. The air-permeability method considers only the external surface whereas the nitrogen adsorption method measures both the external and internal surfaces as shown in Figure 2-21. In summary, this research study indicated that:

1. A negative correlation exists between pozzolanic activity and nitrogen dry specific surface;
2. A positive correlation exists between nitrogen dry specific surface and the carbon content of ash;
3. A negative correlation exists between nitrogen dry specific surface and total silica and alumina content.

The important result is that the strength appears to be inversely correlated to the specific surface as determined by both nitrogen-adsorption and air-permeability. This is not consistant with the generally accepted principle of increased strength with increasing specific surface. The single inverse correlation between specific surface and pozzolanic activity using different sources of fly ashes is actually misleading in the interpretation of test results for this case study since carbon is present and was not considered.

It was found from a correlation study between pozzolanic activity and fineness (by air-permeability) to carbon content ratio that there is a marked correlation as shown in Table 2-44-b and Figure 2-22. The trends are now as anticipated and show the significant effect of carbon

TABLE 2-44

CARBON CONTENT, STRENGTH AND SPECIFIC SURFACES OF FLY ASHES AS DETERMINED FROM AIR-PERMEABILITY, NITROGEN ADSORPTION AND PARTICLE SIZE DISTRIBUTION [15]

A. PROPERTIES

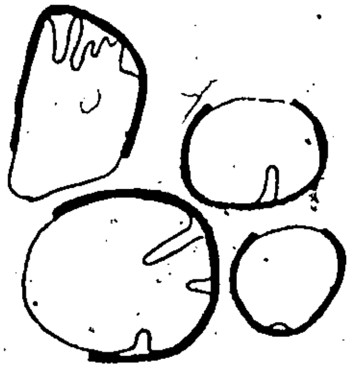
FLY ASH		CARBON CONTENT	SPECIFIC SURFACE (m^2/gr)			
POWER STATION	ASH COLLECTION	(A)	CALCULATED FROM PARTICLE SIZE (B)	AIR PERMEABILITY (C)	N DRY [(a)] (D)	N BURNT [(b)] (E)
Cliff Quay	Boiler and Hopper	4.6	0.081	0.305	4.07	0.76
Earley	Electro-precipitators	8.6	0.097	0.413	3.82	0.87
Ferrybridge	Electro-precipitators	2.5	0.115	0.336	1.02	0.57
Ferrybridge	Electro-precipitators	0.9	0.092	0.209	0.48	1.00
Kirkstall	Boiler and Hopper	25.4	...	0.193	4.70	1.14
Llynfi	Precipitator	53.9	0.102	0.671	8.90	0.67
Portobello	Electro-precipitator	8.3	0.081	0.311	6.50	0.80
Skelton Grange	Electro-precipitator	5.8	...	0.288	1.24	0.68
Stourport	Dust Hopper	2.8	0.080	0.254	0.97	0.66

(a) Determined after the samples had been dried at 110°C.
(b) Determined after the samples had been burnt at 700°C for 6 hours.

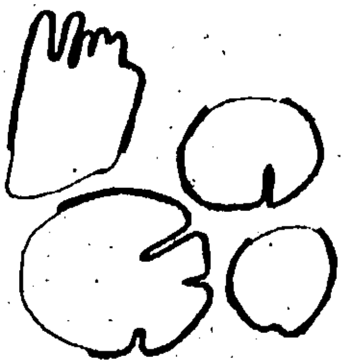
B. COMPRESSIVE STRENGTH

RATIO* $\frac{(C)}{(A)}$	RATIO* $\frac{(D)}{(A)}$	COMPRESSIVE STRENGTH (psi)		
		7 DAYS	28 DAYS	56 DAYS
0.066	0.089	173	324	646
0.048	0.045	221	339	670
0.134	0.041	284	386	1150
0.232	0.053	62	656	1450
0.007	0.018	14	131	643
0.012	0.017	48	83	211
0.037	0.079	27	144	454
0.050	0.214	103	759	2220
0.091	0.346	159	186	420

*(A),(B),(C) and (D) indicate columns of Part A.



(a) Specific Surface Measured by Air-permeability



(b) Specific Surface Measured by Nitrogen Adsorption

FIGURE 2-21 DIAGRAM FOR SPECIFIC SURFACE

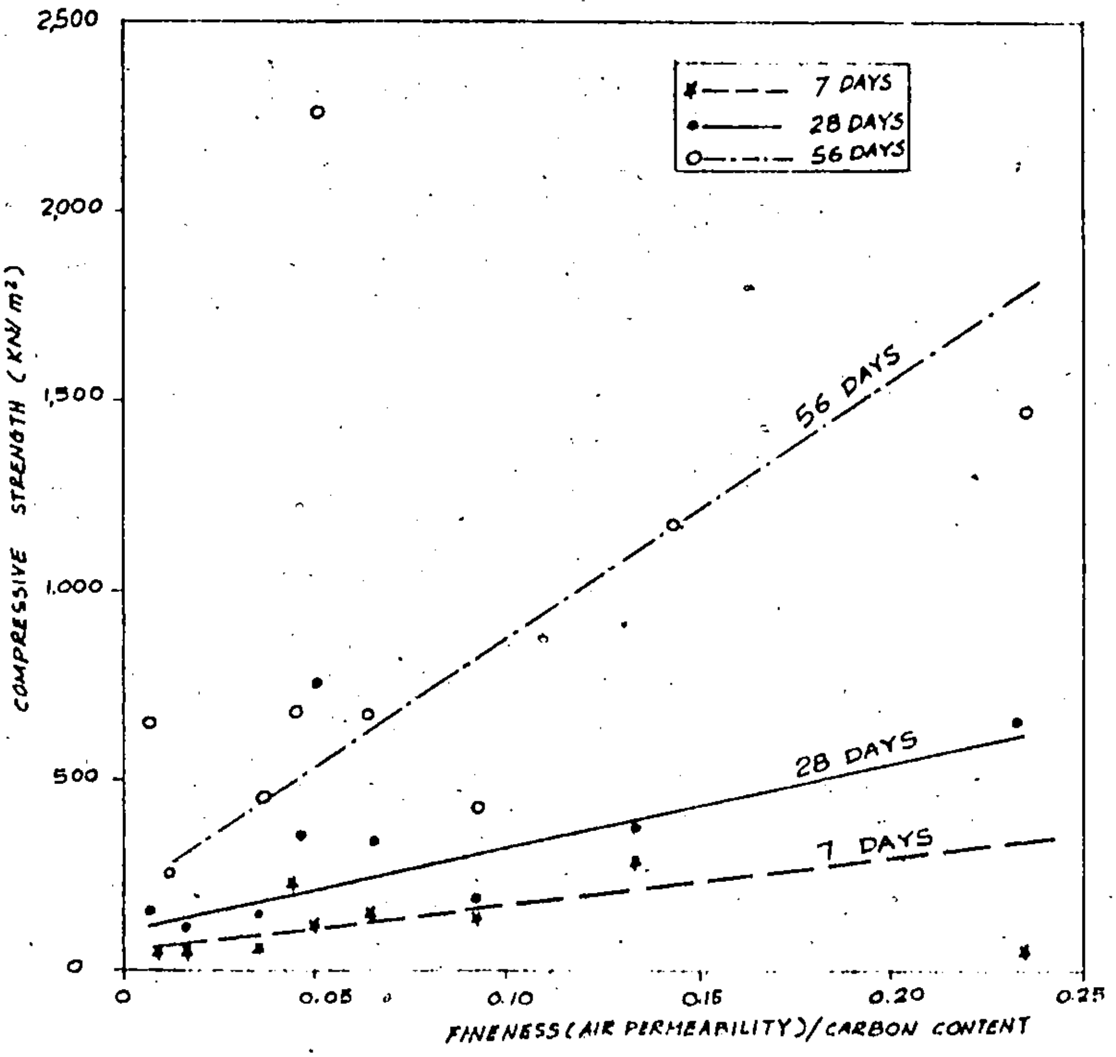


FIGURE 2-22 CORRELATION BETWEEN STRENGTH vs FINENESS/CARBON CONTENT IN LIME-FLY ASH MIX

content on strengths. In this analysis, the air-permeability method gives a more distinctive picture than the nitrogen-adsorption method.

3 TEST PROGRAM, RESULTS AND DISCUSSION

3-1 BASE STABILIZATION

3-1-1 Function of Pavement and Pavement Materials

The basic function of highway pavement structures is to provide a riding surface for the safe operation of vehicles over a defined range of speeds during the anticipated service life of the pavement. Pavements for other transportation facilities - airports, streets, parking lots, etc., - will have similar basic functions. A pavement should be so designed that it can transfer the vehicle loadings to the subgrade with the most economic combination of pavement structure materials for specified conditions such as subgrade strength, geometry of the road, service lift and loadings. The basic structure of a pavement is comprised of the surface course which is in direct contact with the wheel loads and a base which may be a single layer laid directly on the subgrade, or several layers between the surface course and subgrade. The actual pavement structure will depend on how the induced surface stresses are reduced to a level such that the subgrade will not suffer permanent deformation. The materials which make up the various layers in the pavement structure must meet performance requirements related to the function of the particular layer.

For the surface course, the basic requirements are that it safely resist the wear and tear of the wheel loadings, transfer such loadings at a satisfactorily reduced level to lower courses, and survive the destructive influences of the service environment. A simple criteria often adopted is that the minimum compressive strength of surface course materials should be at least six times the maximum anticipated vehicle tire pressure. This criteria is far too simple in that it does not account for the other requirements of the surface course.

For any base material directly on the subgrade, the basic requirement is that the elastic properties of the base material be compatible with those of the subgrade. For normal pavement construction, the elastic modulus of subgrade materials ranges from 2,000 to 10,000 psi. Considering the effect of repeated loadings and the variability of a given material, the desirable range of E values is 20,000 to 100,000 psi for base materials directly on the subgrade. Any other layers of load distributing base material should have an E value of about 200,000 to 500,000 psi. Often, this range of E values can be economically developed by base stabilization methods.

The two conventional materials used for pavement surfaces are portland cement concrete (considered as a rigid pavement since its beam action allows the pavement to bridge over local weak subgrade spots) and asphaltic concrete (considered as a flexible pavement since several layers of base material will be required to reduce the induced stresses to acceptable levels at the subgrade interface). Full depth designs using portland cement concrete or asphaltic concrete are only economic when it is necessary to support heavy wheel loads, to transfer loads onto a much weaker subgrade and/or to maintain structural integrity under severe environmental conditions. However, for a long period, it was really only in the case of asphaltic concrete pavements that load distributing base layers were used between the surfacing and subgrade. It is rather recent practice for portland cement concrete pavements to be treated as layered systems. Previously, any base material utilized was viewed as necessary for protection from pumping and not as a load sharing component of the pavement structure. Presently, most design methods for both types of pavement systems - rigid portland cement concrete and flexible asphaltic concrete - adopt a layered structure in which each component contributes to the satisfactory transfer of vehicle loadings to the subgrade.

Base courses can be compacted layers which use natural or graded aggregates, or stabilized layers in which the aggretates are treated with a binding or cementing material. In general, the shear strength of a soil type material can be expressed by:

$$s = c' + (p-u) \tan \phi'$$

where: s = shear strength of the material;
c' = effective cohesion;
p = total normal stress on failure plane;
u = pore water pressure; and,
ϕ' = effective angle of internal friction.

Thus there are three basic ways of obtaining a significant improvement in the shear strength of a given material, either by increasing the cohesion, the effective normal stress (p-u) between the particles, or the angle of internal friction. When the pore pressure, u, is negligible, the effective normal stress is governed by the overburden and applied loads and is difficult to change. However, the frictional properties can be significantly improved through mechanical stabilization. Compaction is the prime mode of mechanical stabilization and while an important topic, will not be dealt with here. In addition, increased cohesion is obtained by the use of portland cement, asphalt, hydrated lime, and other cementing or modifying materials. Chemical stabilization, which includes both improving the cohesion and changing the engineering properties of base materials is of prime interest here. In particular, the use of pelletized blast furnace slag is examined for this purpose.

3-1-2 Chemical Stabilization of Base Course Materials

Any process that is used to improve the performance of base course materials is called base stabilization. Engineering properties such as strength, stiffness, compressibility, permeability, workability, swelling potential, frost susceptibility and thermal conductivity may be altered by treatments ranging from simple mechanical stabilization to more complete and expensive techniques involving chemical stabilization. The materials to be stabilized, the reason for stabilization and the stabilizing method adopted are not independent and the optimum combination of these factors is judged by the long-term performance and economics of the final stabilized material. A convenient classification of the various chemical stabilization agents and their modes of usage is given in Table 3-1. The base stabilization studies reported here fall into the cementing agent category, namely, slag-cement with some mention of lime-fly ash.

TABLE 3-1

STABILIZING AGENTS AND PROCESSES

(Table organized from the general literature on base stabilization)

TYPE OF AGENT	AGENT	PRIMARY MECHANISM OF STABILIZATION	MOST SUITABLE MATERIALS (SOIL) TO STABILIZE	METHOD
Cementing	portland cement	hydration; some modification of clay minerals.	sandy soil, granular materials, low plasticity clay (lean clays).	lean concrete (cement stabilized aggregate), soil-cement, plastic soil cement. soil-cementation.
	lime	change water film, flocculation, agglomeration, chemical, pozzolanic reaction.	granular materials, lean clay.	
	lime-fly ash	pozzolanic reaction; some modification of clay mineral.	granular materials, lean clay.	lime-fly ash-aggregate.
	slag-cement or other metallurgical cements	hydration.	granular materials.	slag-cement-aggregate.
	bitumen	binding properties of asphalt cement.	granular materials, sandy soil.	sand-gravel bitumen, macadam, sand bitumen.
Modifier	cement	modification of clay; change water film.	clay.	cement-modified soil.
	lime	change water film, ion exchange, modification of clay minerals.	clay.	soil-modification.
	bitumen	retard moisture absorption.	silts, cohesive soils.	soil-bitumen.
Waterproofing	bitumen	retard moisture absorption, coating soil grains.	sandy-clay soil.	soil-bitumen, sand-bitumen.
Water-retaining	calcium chloride or sodium chloride	deliquescent properties; lower freezing point; base exchange.	graded aggregate (arid, dry).	road mix, spray.
Miscellaneous chemicals	resin		limited to special applications.	special design.
	calcium acrylate sulphite lignin	...		

3-1-3 Details of Materials Used in Base Stabilization Studies

Granular A blast furnace slag, pelletized slag, lime, fly ash, calcium chloride and natural aggregates were used in the base stabilization studies. The basic properties of these materials will be detailed before examining the tests and results.

3-1-3-1 Granular A Blast Furnace Slag

This air-cooled blast furnace slag is processed and marketed by National Slag Limited in Hamilton and originates from both STELCO and DOFASCO. The blast furnace slag has a bulk specific gravity of 2.3 and the typical gradation shown in Table 3-2. The gradation has some variation from time to time during production so that a controlled gradation has been used throughout the base stabilization studies as follows: 27% retained on the 3/8" sieve; 23% passing the 3/8" sieve and retained on the #4 sieve; and, 50% passing the #4 sieve. The chemical composition of blast furnace slag supplied by STELCO is shown in Table 3-3 [52]. This is typical of that for the test program.

TABLE 3-2

GRADATION OF GRANULAR A

SIEVE SIZE	% PASSING	% RETAINED
3/4"	99.2	27.5
3/8"	72.5	
#4	49.5	23.0
#8	31.2	49.5
#16	19.2	
#30	12.7	
#50	7.7	
#100	4.4	
#300	1.9	

TABLE 3-3

CHEMICAL COMPOSITION OF BLAST FURNACE SLAG

COMPOSITION		PERCENT
Calcium Oxide	CaO	38.6
Silicon Dioxide	SiO_2	34.9
Aluminium Oxide	$A\ell_2O_3$	10.0
Magnesium Oxide	MgO	13.7
Iron Oxide	FeO, Fe_2O_3	0.64
Manganese Oxide	MnO	0.19
Sulphur	S	Not determined*

* Generally 1.5% to 2.5%

3-1-3-2 Pelletized Slag (or pellets)

Pellets are categorized between expanded slag and granulated slag because they have a lower specific gravity than the 2.3 of air-cooled slag, and are often a glassy substance similar in properties to granulated slag. The main purpose in pelletizing the slag is to produce a lightweight aggregate for use as fine aggregate in structural concrete and masonry units. A typical gradation for the pellets is shown in Table 3-4. This gradation also has variability between batches. All of the pellets used for compressive strength test specimens have been controlled to the gradation: 50% passing the 3/8" sieve and retained on the #16 sieve; and, 50% passing the #16 sieve and retained on the #200 sieve. The portion passing the #200 sieve was separated in order to control the amount of net fines (-#200) in the various mixes. Initially, these pellets were developed as a lightweight aggregate and the cementing properties of ground pellets were not utilized. Based on some field evidence of self-cementing, referred to in Section 2-3-2, and some preliminary work, it appeared possible that a base stabilization process could be developed using ground pellets. The energy advantages of such a usage have been clearly indicated in Section 2-3-1.

TABLE 3-4

TYPICAL GRADATION OF PELLETS

SIEVE SIZE	% PASSING	% RETAINED
3/8"	100.0	62.5
#4	98.7	
#8	74.0	
#16	37.5	37.5
#30	12.8	
#50	4.2	
#100	1.7	
#200	0.9	

3-1-3-3 Lime

Commercial grade, high calcium, hydrated lime was used as supplied by Domtar Chemical Limited of Toronto from their Beachville operations (Beachville Chemical Hydrate). Its chemical analysis and physical properties are shown in Table 3-5.

3-1-3-4 Calcium Chloride

Commercial grade calcium chloride, $CaC\ell_2$ (77%-80% flake), supplied by Allied Chemicals of Canada Limited, was used. It was added in solution form by dissolving in water.

3-1-3-5 Fly Ash

Fly ash obtained from the Ontario Hydro beneficiating plant at Lakeview Thermal Plant was used. The analysis of the ash showed 8.31% carbon (loss on ignition) and 95% passing the #325 sieve.

3-1-3-6 Natural Aggregates

Crushed limestone aggregate from Canada Crushed and Cut Stone Limited (normally used for portland cement concrete) adjusted to the same gradation as the granular A was used in compressive strength specimens to replace the granular A. Lake Ontario beach sand from the same supplier (normally used for portland cement concrete) controlled to the same gradation as the pellets was used to replace the pellets in other specimens.

TABLE 3-5

CHEMICAL ANALYSIS AND PHYSICAL PROPERTIES OF HYDRATED LIME

(Data supplied by DOMTAR)

CHEMICAL ANALYSIS		Percent
Compounds		
Silicon Dioxide and Insolubles	SiO_2	0.50
Ferric Oxide	Fe_2O_3	0.10
Alumina	Al_2O_3	0.30
Sulphur	S	0.06
Magnesium Oxide	MgO	0.60
Calcium Oxide	CaO	73.80
Available Lime Index as Calcium Oxide	CaO	71.50
Available Lime Index as Calcium Hydroxide	$Ca(OH)_2$	94.50
Carbon Dioxide	CO_2	0.90
Moisture	H_2O	1.00
Unhydrated Oxides	...	0.40

TABLE 3-5 (Continued)

PHYSICAL PROPERTIES			
Density	loose	24	pcf
	packed	36	pcf
Blaine fineness		13,000	cm^2/gr
Sieve analysis			
	sieve size	% passing	
	#50	100	
	#100	99.9	
	#200	96.0	
	#325	93.0	

3-1-4 Experimental Program

3-1-4-1 Test Schedule

The research was largely restricted to a laboratory investigation of the stabilization of base courses using hydraulic slag fines ground from pellets. Granular A and pellets with the gradations given in the previous section were selected as the base material to be stabilized. This choice was governed by some examples of cementing during storage at National Slag Limited and the presence of some free lime with the slag that would assist any cementing reactions. The nature of the cementing reaction and base stabilization development was examined in some detail. In addition, some initial work on autoclaved pellet fine bricks was completed to the trial stages. The test program consisted of six steps as summarized in Table 3-6.

TABLE 3-6

EXPERIMENTAL PROGRAM FOR BASE STABILIZATION STUDY

STEP	PURPOSE
1	Cementing properties of ground fines from pellets. Pozzolanic reaction of fly ash-lime-granular A mixes. $CaC\ell_2$ effect on strength gain.
2	Glass content of pellets.
3	Effect of amount of fines on strength development. Strength gain from ground pellets.
4	$CaC\ell_2$ and Blaine fineness of fines effect on strength gain.
5	Optimum lime content for strength development. Catalysis effect of portland cement on slag fines:
6	Strength gain by autoclave curing of stabilized base specimens and bricks.

3-1-4-2 Test Procedures

Materials Preparation

Granular A and pellets, when used as aggregates, were first dried at room temperature and then their gradations controlled as previously indicated. The fines were prepared either in a stone ball mill or in a modified Los Angeles abrasion machine.

1. Stone Ball Mill Method - pellets charged into ceramic drum with stone balls, called BM fines.
2. Modified Los Angeles Abrasion Machine Method - pellets charged into Los Angeles abrasion machine with steel balls, called LA fines.

Detailed grinding processes for both methods are shown in Table 3-7.

Test Methods

The raw materials and prepared materials were tested according to the standard methods specified by ASTM or AASHO, where suitable methods have been developed. Test methods which are not designated by these standards associations are found in the appendix or readily available references. A list of the test methods used during the research is given in Table 3-8.

Preparation of Specimens for Compressive Strength

Four-inch diameter modified Proctor specimens were prepared according to ASTM C593-69 (5 layers,10 lb hammer, 18 in. drop, 25 per layer).

TABLE 3-7

PELLET GRINDING PROCESSES

METHOD		STONE BALL MILL	MODIFIED LOS ANGELES ABRASION MACHINE
Charge	ball	315 stone balls, size range 1/2"-3/4" sieve	20 steel balls of one inch diameter
	material	about 5 pounds	about 20 pounds
Drum size		7 1/2" Diameter, 7 1/4" Length Cylindrical Ceramic Drum	28" Diameter, 20" Length Hollow steel cylinder closed both ends
Drum speed		60 rpm rotated with the axis in horizontal position	30 rpm rotated with axes in a horizontal position
Remarks		Individual particles are ground by relatively light stone and rough inside surface of drum.	Particles are pulverized by steel balls to finer and finer particles. This machine is designed for ASTM C131 or AASHO T96 Tests.

TABLE 3-8

TEST METHODS

(Current ASTM or AASHO Procedure Used Where Available)

NO.	TEST	MATERIAL TESTED	METHODS USED
1	Glass Content	pellets	Appendix
2	Optimum Moisture Content	aggregate	ASTM D1557, AASHO T180
3	Specific Gravity of Fines	fines, cement	ASTM C188, AASHO T133
4	Fineness of Fines	fines, cement	ASTM C204, AASHO T153
5	Ultra Violet Light Test	pellets	Appendix
6	Brick Test	brick	ASTM C67, AASHO T32
7	Compressive Strength Test	stabilized base	ASTM C593
8	Cubic Specimen Test	mortar specimen	ASTM C109 and C595
9	pH Test	steel slag	Fisher Universal pH Indicator Chart or Hydro pH Paper Dispenser, Micron Essential Lab. Inc.
10	Centrifugal Kerosene Equivalent	aggregate	Test Method No. Calif. 303-B
11	Sand Equivalent Test	aggregate	ASTM D2419, AASHO T176
12	Specific Gravity of Fine Aggregate	aggregate	ASTM C128, AASHO T84
13	Specific Gravity of Coarse Aggregate	aggregate	ASTM C127, AASHO T85
14	Specific Surface	aggregate	Test Method No. Calif. 303-B
15	Sieve Analysis of Fine or Coarse Aggregate	aggregate	ASTM C136, AASHO T27
16	Sampling Stone, Slag, Gravel, Sand, and Stone Block for Highway Material	aggregate	ASTM D75, AASHO T2
17	Amount of Material Finer than #200 Sieve in Aggregate	aggregate	ASTM C117, AASHO T11
18	AC Content in Emulsified Asphalt	asphalt	ASTM D244, AASHO T59
19	Penetration Test on Residue AC	asphalt	ASTM D5, AASHO T49
20	Wet Track Abrasion Test (WTAT)	slurry seal	[24,26]
21	Young Consistency Test	slurry seal	[26]
22	Slurry Seal Setting Time Test	slurry seal	Chevron Test Method [30]
23	Slurry Seal Setting Test	slurry seal	Chevron Test Method [30]
24	Stick Test	slurry seal	[26]

The modified Proctor optimum water content was found to be 10% at a dry density of 129 pcf for the mix proportions used: 70% granular A; 18% pellets; 10% fines; and, 2% lime. It was found best to control the water content on the basis of no slump since the mix is too coarse for normal Proctor procedures. The optimum water content was not very sensitive to mix proportion changes. Upon finishing the compaction and leveling the compacted surface, the specimen was removed from the special split mold, then sealed in double plastic bags, and cured at 100°F in an oven for the specified time. Sealed curing insures that moisture is maintained for any reactions. After curing, the specimens were capped on both ends with hydrostone. Three specimens were made and the results averaged for each test mix unless otherwise indicated.

3-1-4-3 Test Results and Discussions

Step 1: Cementing Properties, Pozzolanic Reaction, $CaC\ell_2$ Effects

Previous exploratory work which used the granular A and pellets without prepared fines had not produced the desired compressive strength of 500 psi after seven days sealed curing at 100°F [19]. For this reason, Test step 1 focussed on a preliminary investigation of slag stabilized base using prepared fines as a cementing binder material, pozzolanic reactions of lime and fly ash, and calcium chloride effects on strength gain. The test results from this investigation are shown in Table 3-9.

The main trends observed from these test results are:

TABLE 3-9

TEST RESULTS FOR PRELIMINARY INVESTIGATION

PURPOSE		STRENGTH WITHOUT LIME		STRENGTH WITH LIME			POZZOLANIC REACTION	$CaCl_2$ EFFECT		NATURAL AGGREGATE	
TEST SERIES		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Materials (%)	Lime	...	...	2	2	2	2	2	...	...	...
	Fly Ash	...	2	...	...	...	10	...	...	...	...
	BM Fines (a)	10	10	10	10	...	...	10	10	5	5
	Natural Fines (b)	...	...	...	...	10	...	...	...	...	...
	$CaCl_2$	...	...	...	...	...	...	2	2	...	...
	Pellets	20	18	18	18	18	18	18	18	...	25
	Granular A	70	70	70	70	70	70	68	70	70	...
	Crushed Stone	...	...	...	...	...	...	...	...	...	70
	Beach Sand	...	...	...	...	...	...	...	...	25	...
Water Content (%)		10	10	10	7	10	10	10	10	10	10
Curing Days at 100°F		7	7	7	7	7	7	7	7	7	7
Compressive Strengths (psi)		2690	2140	1440	1587	850	1360	1650	2330	1360	1400
Remarks		green colour	...	green colour	slight green colour	no green colour	...	...	...	green colour	green colour

(a) prepared by stone ball mill, having Blaine fineness of 2000 cm^2/gr.
(b) Natural fines are fines which passed #200 sieve from the unground raw pellets, having Blaine fineness of 1000 cm^2/gr.

1. The compressive strength for the various test series incorporating fines prepared with the stone ball mill are from 1,440 to 2,690 psi, much higher than the aim compressive strength of 500 psi. Test series No. 1 which contained no lime gave the highest strength development of 2,690 psi. This series of preliminary test results clearly indicated that the ground pellets possessed cementing properties under appropriate curing conditions and that lime additions were probably not necessary. As such, the preliminary investigation was the groundwork and motivating factor for much of the research that followed.
2. The results of test series Nos. 3 and 5 indicate that the natural fines are much inferior to the ball mill fines in strength development. This was anticipated since the Blaine fineness of the ball mill fines is higher than that of the natural fines. The higher Blaine fineness will contribute to the stabilization potential of the fines.
3. The addition of lime or $CaC\ell_2$, which generates Ca^{++} ions in solution, did not help the strength gain in the specific proportions used. This indicates that the ground fines from the pellets have self-cementing properties through hydration processes producing a cementing gel, whereas pozzolanic reactions occur between siliceous pozzolans and lime, both of which are indispensable components to the reaction. The amount of lime added was very high at 20% of the fines resulting in a drop of

strength that may not occur for lower lime additions. Thus, there may still exist an optimum lime content at which the maximum strength is produced.

4. Test series No. 6 did not involve fines, but depended on the pozzolanic reaction between lime and fly ash (not beneficiated, i.e. high in carbon, ≈ 13%) for strength development. The compressive strength of 1,360 psi developed is well above the required minimum of 500 psi and indicates the potential for such a base stabilization process. Since it would appear that the Poz-O-Pac Company [103] has development rights to this process, it was not proceeded with.
5. The amount of fines used for the test series was fairly high and generally not economical. From this it was concluded that the next test series should involve determining the mix which is closest to the desired minimum strength of 500 psi after seven days, 100°F sealed curing, and the relation between amounts of fines and strength gain.
6. Instead of using slags (granular A and pellets) as aggregate, crushed stone was used to replace granular A and beach sand to replace pellets in test series Nos. 9 and 10 to check the effect of strength gain with natural aggregates. It was found that there was a significant reduction in the strength developed (approximately 1/2) compared to the use of slags in test series Nos. 1 and 2. However, more than adequate strength was still developed to meet specifications. The water content was somewhat reduced since the natural aggregate

tended to be less porous.

7. After failing the specimens, a green colour and sulphur smell was detected which provided evidence on the maturity of the reaction or hydration. Specimens which had lower strengths tended to have less colour and smell than the stronger specimens. This indicates that the pellets contain sulphide in some form of CaS and in the well cured condition polysulphides are formed with the emission of hydrogen sulphide (H_2S).

Step 2: Glass Content

The cementing properties of fines ground from pellets are contributed by the latent potential energy of glassy substances, fineness of ground material and chemical composition of pellets used [43]. The glass content of the pellets was determined with a light microscope for both the total gradation and for each separate particle size group by the procedure given in Appendix 2-2. In order to see if there were any preferential crushing effects on particle size and glass content, pellets were first crushed down to various micro-sizes, such as passing the #50 sieve and retained on the #100 sieve, #100 to #200, #200 to #300, #300 to #400 and passing the #400 sieve. Each of these size groups was then examined for glass content with the results shown in Table 3-10.

Next, the glass contents of pellets from various processes which could effect the basicity ratio (defined according to the formula $(CaO + MgO)/(SiO_2 + Al_2O_3)$) were determined. These glass content results are summarized in Table 3-11 and Figure 3-1.

TABLE 3-10

MICRO SIZE EFFECT ON GLASS CONTENT OF PELLETS

PELLET NUMBER	GLASS CONTENT OF TOTAL GRADATION					
	#50-#100	#100-#200	#200-#300	#300-#400	-#400	Average
7	87	88	90	90	88	88
10	30	32	40	35	30	34
1	...	...	37	35	...	36
2	...	...	26	22	...	24
3	82	...	92	89	91	90
4	...	...	89	90	...	90
5	...	...	42	41	...	42
6	56	...	65	64	69	65
S	61	67	82	77	78	73

* #50-#100, for example, means particles group passing #50 sieve and retained on #100 sieve.

TABLE 3-11

BASICITY EFFECT ON GLASS CONTENT OF PELLETS

PELLET NUMBER	BASICITY	GLASS CONTENT OF #200-#300							
		3/8	3/8-#4	#4-#8	#8-#16	#16-#30	#30-#50	-#50	TOTAL GRADATION
106	1.06	56	86	96	100	97	99	90	94
107	1.07	...	...	...	...	...	...	...	97
112	1.12	...	...	...	...	...	...	...	100
114	1.14	...	...	...	...	...	...	...	99
118	1.18	92	97	100	100	99	100	100	100

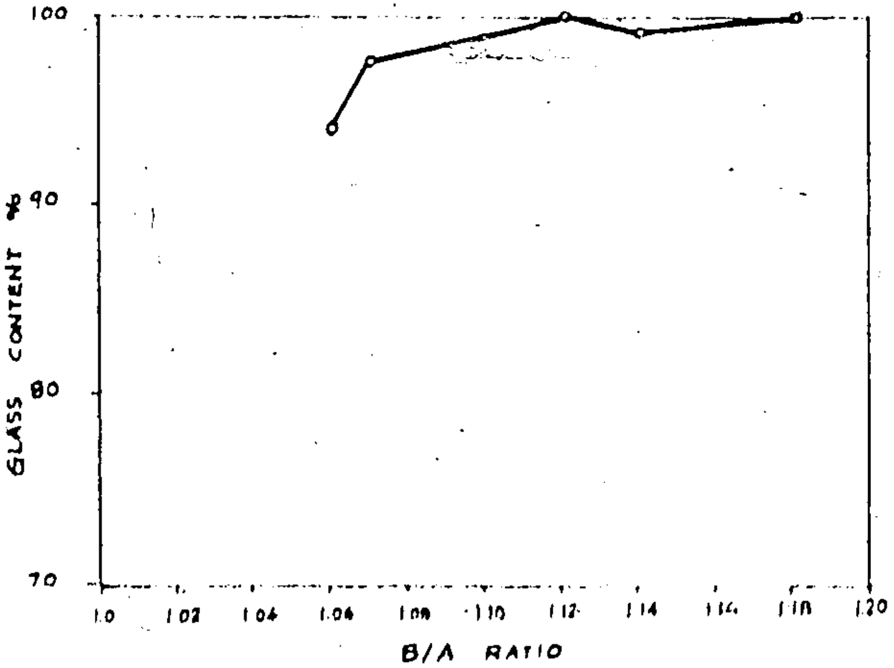


FIGURE 3-1 B/A RATIO vs GLASS CONTENT OF PELLETS

Finally, for a given pellet type, the glass content vs grain size was investigated in order to find the granulating efficiency of different particle size distributions. These comparisons are given in Table 3-12 and Figures 3-2 and 3-3.

These glass content results indicate:

1. The glass contents for specimens made from various portions of fines such as #50 to #100 sieve size, #100 to #200, and -#400 fell into a fairly narrow range for each pellet type examined. This indicated that glass contents determined for portions of fines in the range of -#200 to #400 are representive and reliable. Since larger and smaller sizes than #200 to #300 give some difficulty in determining the actual glass portion of each particle, the glass content determinations were standardized to the #200 to #300 size group of particles.
2. The results in Table 3-12 indicate that the glass content increases as the basicity ratio rises. However, the variation of glass content with basicity ratio for the pellet samples tested is very narrow, ranging fron 94% to 100% for a basicity ratio range of 1.06:1.18. These results are not concordant with the general concept that higher lime contents in slag make the slag harder to granulate, i.e., easier to crystallize with lower glass content. The temperature control from molten slag to cooling should be considered in addition to basicity ratio effects on the granulation process.

TABLE 3-11

GRAIN SIZE EFFECT ON GLASS CONTENT

PELLET NUMBER	GLASS CONTENT (%) OF #200-#300							
	Total Gradation	+#4	#4-#8	#8-#16	#16-#30	#30-#50	#50-#100	-#100
18	94	76	86	88	93	95	91	83
19	81	65	75	80	81	79	80	68
22	80	65	73	83	90	84	82	71
25	78	58	66	75	84	90	78	61
26	77	70	71	82	91	90	80	65
35	89	84	89	89	95	95	86	72
8	74	69	54	75	88	90	75	60

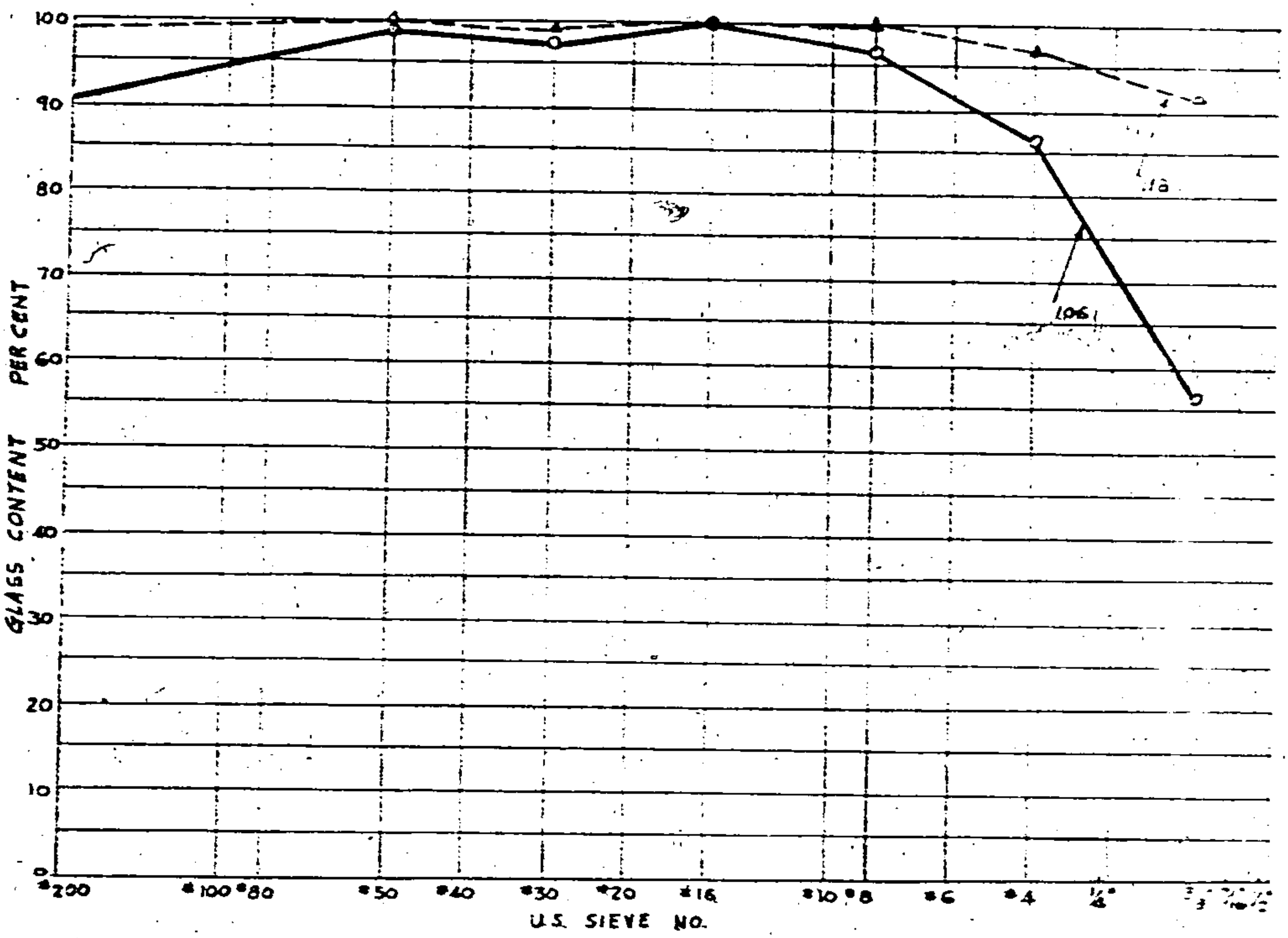


FIGURE 3-2 GLASS CONTENT vs GRAIN SIZE FOR 118 AND 106 SAMPLES

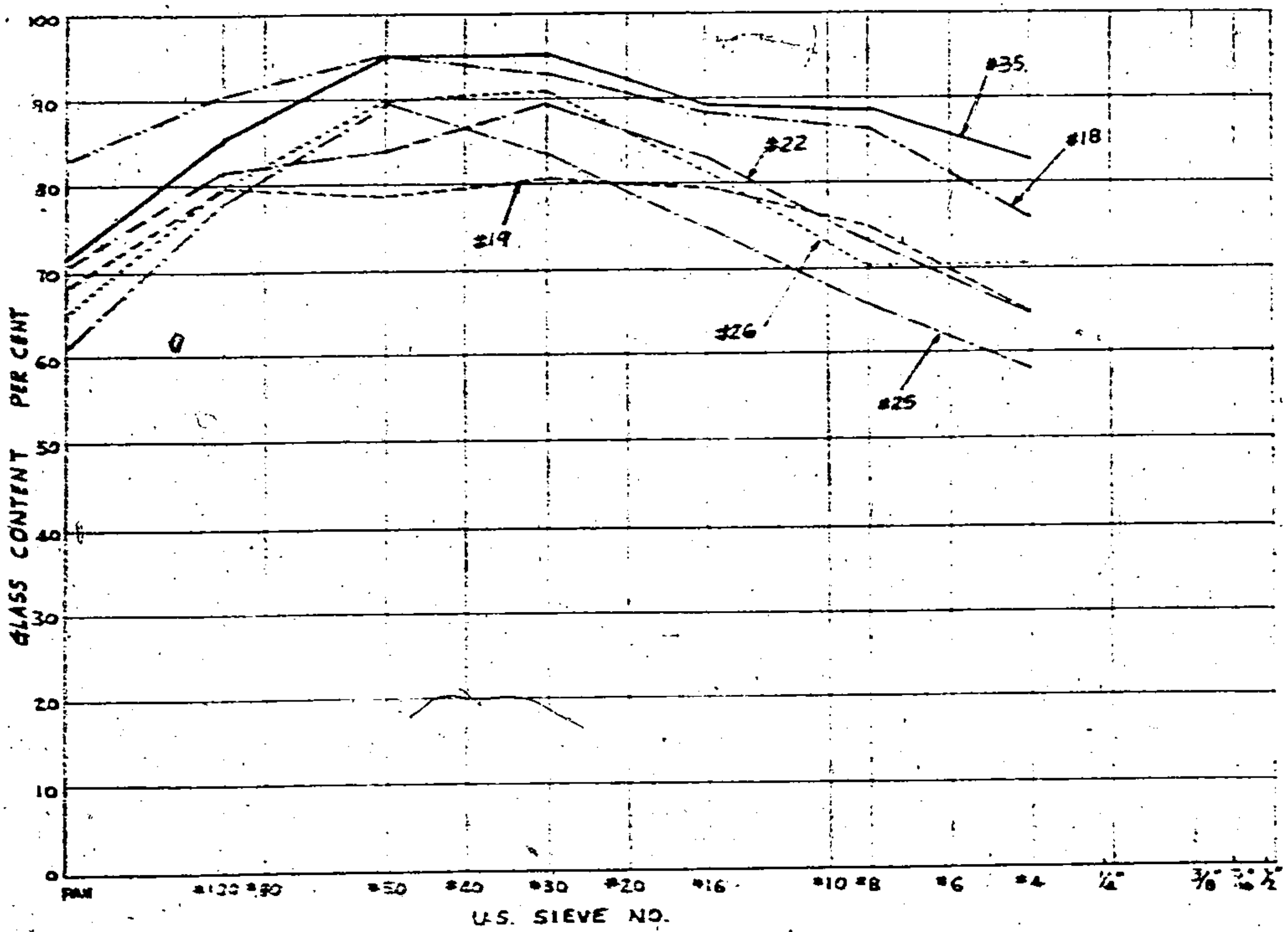


FIGURE 3-3 PARTICLE SIZE vs GLASS CONTENT

3) The test results in Table 3-12 and Figure 3-2 (from Table 3-11) and 3-3 show that the pellet particles passing the #16 sieve and retained on the #50 sieve (shaded area on Table 3-12) give the optimum size range for granulation. Generally, particle sizes outside this range give lower glass contents, indicating that there is an optimum pellet weight and cooling surface. This knowledge will allow selective screening of the pelletized slag to get higher glass contents. However, there may be some self-cementing of the finer sizes that lowering their measured glass content.

Step 3: Amount of Fines Required

The effect of a fines content of strength gain was determined for a fines content range of 2% to 25% by total weight. In this test series, the water content of each specimen was 10% and the curing condition was seven days sealed at 100°F. These test results are given in Table 3-13 and Figure 3-4.

Instead of using the fines ground from pellets and unground pellets separately to make up the mixes, the total gradation of ground pellets from various grinding times were used in the mixes. This was done to check if there were any significant effects on strength gain of portions of such ground pellets in addition to fines passing the #200 sieve. These ground pellets were prepared in a modified Los Angeles abrasion machine with grinding times of one, three, six and twelve hours. Gradations of the resulting products are shown in Table 3-14. The strengths of seven, fourteen, and twenty-eight day specimens prepared with these ground pellets from various grinding times are

TABLE 3-13

FINES CONTENT EFFECT ON COMPRESSIVE STRENGTH

NO. OF TEST	2	3	4	5	7	10	15	20	25
Proportion (%)									
Granular A	70	70	70	70	70	70	70	70	70
Pellet	28	27	26	25	23	20	15	10	5
Fines (a)	2	3	4	5	7	10	15	20	25
Strength (psi)	600	697	1150	1270	1740	2690	3360 (b)	4260 (b)	5070 (b)
Remarks	No colour	No colour	slight green colour	green colour, sulphur smell	green colour, sulphur smell	green colour, sulphur smell	green colour, sulphur smell	green colour, sulphur smell	green colour, sulphur smell

(a) Fines made from pellets in stone ball mill. Glass content 47% and fineness of 3430 cm^2/gr.
(b) Strength is average for two specimens.

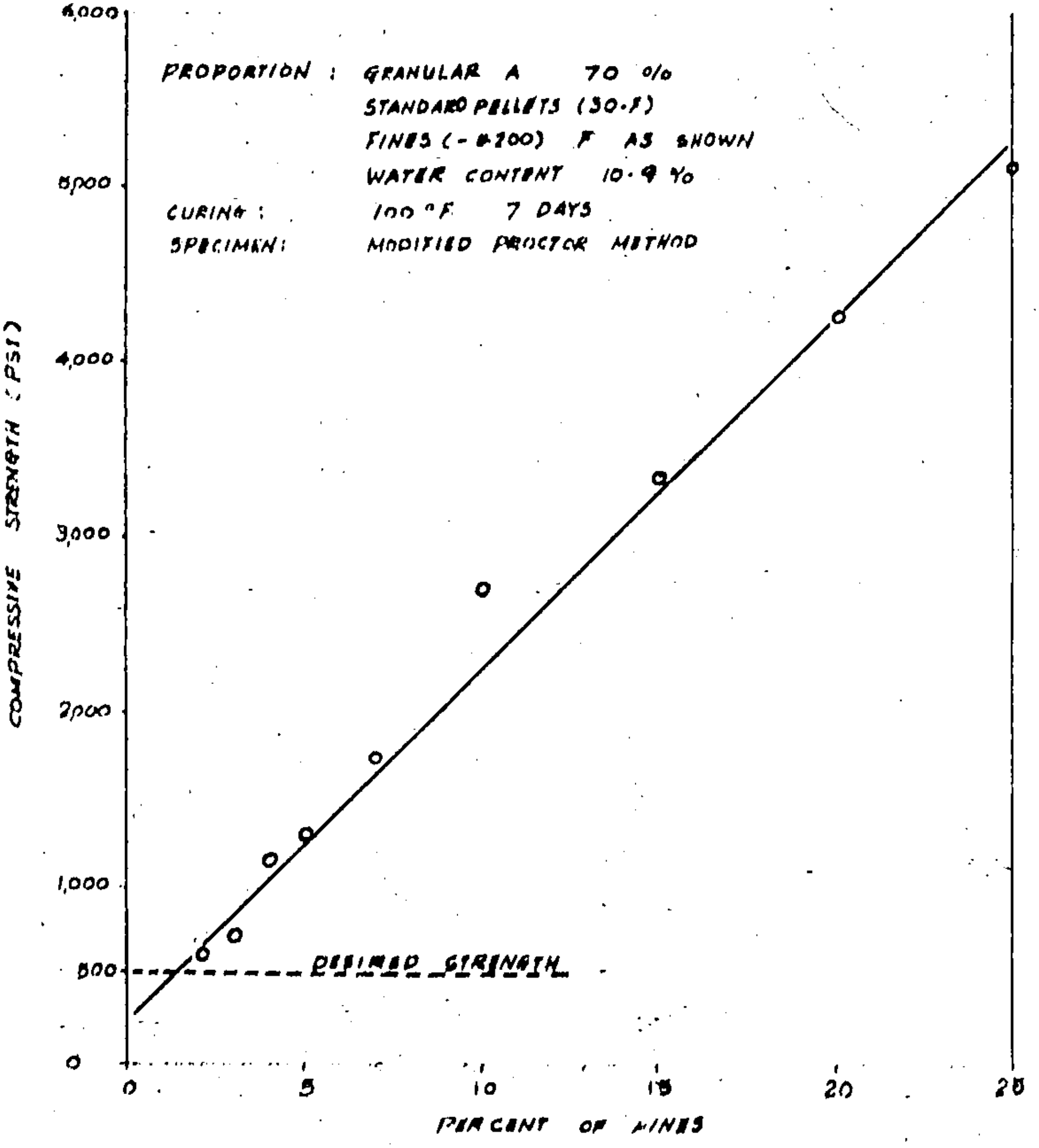


FIGURE 3-4 PERCENTAGE OF FINES
vs COMPRESSIVE STRENGTH

TABLE 3-14

PROPERTIES OF PELLETS GROUND IN LOS ANGELES ABRASION MACHINE

NO. OF GROUND PELLETS		G0	G1	G3	G6	G12
Charge	Pellets (gr)	10000	10000	10000	10000	10000
	1" Steel Ball	20	20	20	20	20
	2" Steel Ball	6	6	6	6	6
Grinding (hours)		No grinding	1	3	6	12
% of Fines Passing #200 Sieve		0.9	7.0	10.5	18.5	39.8
Fineness of Fines (cm^2/gr)		Not tested	1910	2100	2200	2170
Gradation % Passing	3/8 sieve	100.0	100.0	...	...	...
	#4	98.7	100.0	100.0	...	...
	#8	74.0	98.5	99.9	100.0	...
	#16	37.5	73.8	92.6	99.0	100.0
	#30	12.8	37.4	65.3	77.2	98.0
	#50	4.2	20.6	44.1	55.5	78.3
	#100	1.7	11.8	25.2	34.8	57.8
	#200	0.9	7.0	10.5	18.5	39.8

TABLE 3-15

COMPRESSIVE STRENGTH OF SPECIMENS MADE FROM GROUND PELLETS

TEST SERIES			GT-1	GT-3	GT-6	GT-12
Proportion (%)	Granular A		70	70	70	70
	Ground Pellets (See Table 3-14)	G1	30	...	...	...
		G3	...	30	...	...
		G6	...	...	30	...
		G12	...	...	...	30
Water Content (%)			10	10	10	10
% of Net Fines			2.1	3.2	5.6	11.9
Strength (psi) (a)		7 days	750	1660	1950	2120
		14 days	1110	1920	2170	2370
		28 days	1030 (b)	2120	2680	2740

(a) Average of two specimens.
(b) This strength was erratic.

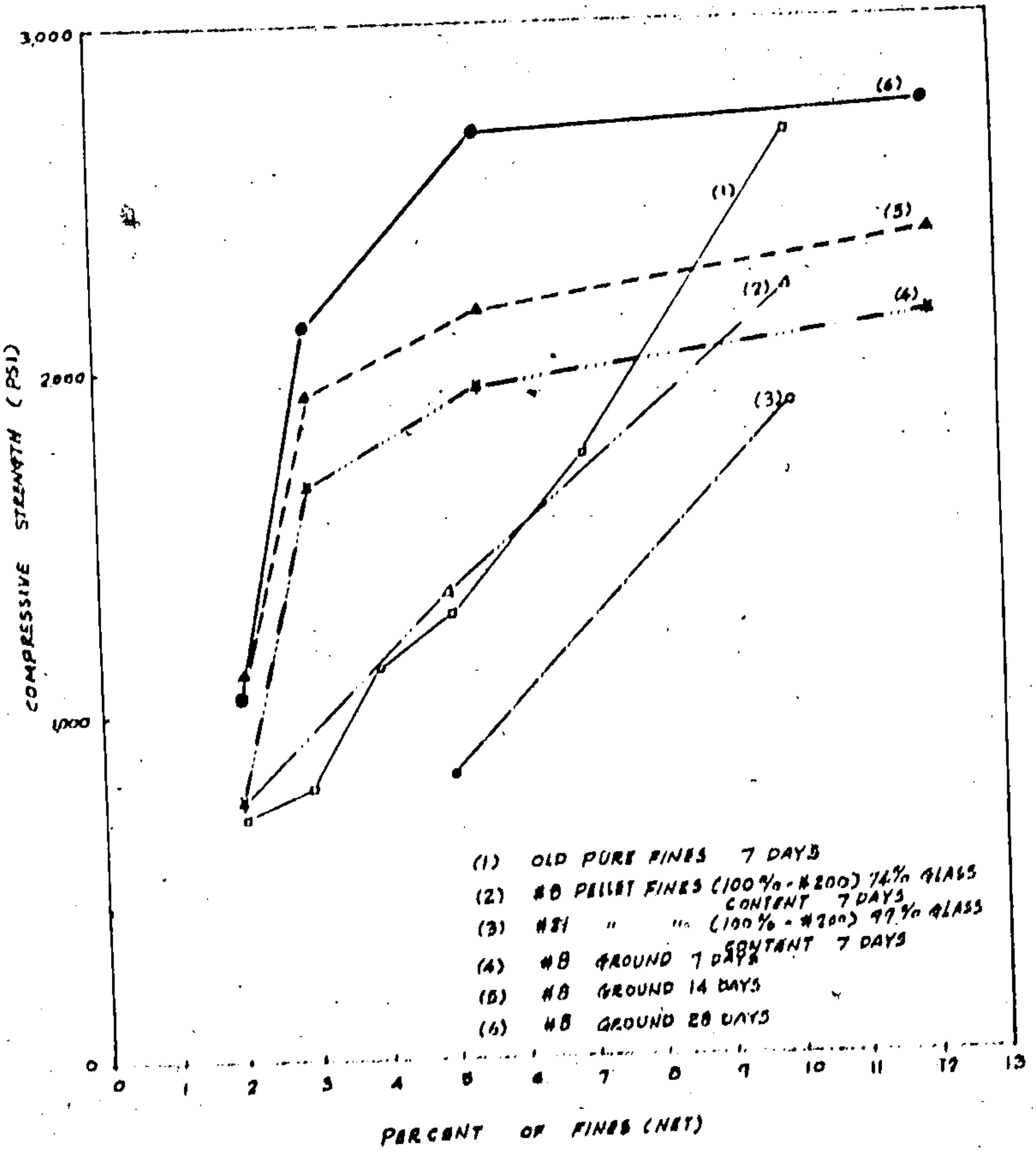


FIGURE 3-5 AMOUNT OF FINES vs STRENGTH

shown in Table 3-15 and Figure 3-5.

In addition, fines were prepared in the modified Los Angeles abrasion machine by totally grinding pellets to -#200. These fines had a Blaine fineness of 2850 cm^2/gr. Compressive strength specimens were made using 2%, 5% and 10% of these fines in order to compare with the strengths of total gradation ground pellets found in the previous test series. The test results are shown in Table 3-16 and also in Figure 3-5.

These results indicated the following grinding effects on strength:

1. It was found that the compressive strength increases approximately linearly with increasing -#200 fines in the specimen as shown in Table 3-13, Figure 3-4 and Table 3-16. It should be noted that the fines for all of these specimens were prepared from the same type of pellet supplied over a period of time that should be extremely similar in chemical and physical properties. The mix which had the compressive strength closest to the "aim" of 500 psi was found to be the one containing approximately 2% fines, a fairly low figure when compared to other base stabilization methods.
2. The test results for compressive strength specimens prepared from the total gradation of ground pellets as shown in Table 3-15 and Figure 3-5 indicate that for the range of net fines content from 2% to 9%, the strength of such specimens is higher than that of a comparable specimen made from totally ground fines, unground pellets and granular A. Outside of this range,

TABLE 3-16

COMPRESSIVE STRENGTH FOR TOTALLY GROUND FINES (-#200)

NO. OF TEST SERIES		GTT-2	GTT-5	GTT-10
Proportion (%)	Granular A	70	70	70
	Pellets (unground)	28	25	20
	Fines (totally ground	2	5	10
Strength (psi)	7 days	760	1340	2190

the strength development begins to show the opposite trend. These results can be explained in the following ways:

(a) Not only the -#200 fines in the total gradation of ground pellets, but also fines coarser than #200 contribute to the strength gain. This may be due to the formation of "fresh", more active, surfaces during grinding.

(b) The opposite trend outside the range of 2% to 9% net fines could be caused by a poor gradation (too fine) due to over-grinding of pellets. This could have an adverse effect on the grading density and also result in zones deficient in water for adequate curing.

3. In general, the longer curing of fourteen and twenty-eight days increased the strengths by 11% to 15% and 28% to 37%, respectively. It is possible that at longer curing times additional water may be necessary for hydration that was not always available. The twenty-eight day strengths are not substantially better than the seven day, indicating the reaction proceeds fairly rapidly at 100°F. Obviously, the effect of curing at normal temperatures should be checked on a field scale.

Step 4 $CaC\ell_2$ and Fineness of Fines

The effect of $CaC\ell_2$ on compressive strength gain for several curing periods was investigated using specimens with the composition given in Table 3-17. The 2% $CaC\ell_2$ was dissolved in water before mixing.

These test results are shown in Table 3-17 and Figure 3-6.

Glass content and fineness effects on strength development were investigated using 2%, 5% and 10% fines ground from different pellets in the stone ball mill. Specimen details and test results are shown in Table 3-18.

The effect of $CaC\ell_2$ and fineness of fines can be summarized as:

1. It was found that there tends to be an adverse effect on compressive strength development with $CaC\ell_2$ additions. This is opposite to the general behaviour anticipated from portland cement concrete research. There was very little difference in compressive strength development between the specimens containing no $CaC\ell_2$ and 2% $CaC\ell_2$ at three days and twenty-eight days curings. However, in the three to twenty-eight days curing period, the compressive strength specimens prepared with 2% $CaC\ell_2$ showed much lower strengths than those with no $CaC\ell_2$. These trends show up clearly in Figure 3-6. In general, it would appear that the addition of $CaC\ell_2$ is not helpful to the pelletized slag stabilization process. Since a high concentration of $CaC\ell_2$ was used, future work on lower $CaC\ell_2$ usage might show parallel trends to portland cement concrete observations.
2. The general concept that increasing the glass content and/or Blaine fineness of ground pellets improves the compressive strength development was not shown in the rather erratic test results reported in Table 3-18. There may exist an optimum condition for formation of the glassy phase in the pelletized

TABLE 3-17

EFFECT OF $CaCl_2$ ON STRENGTH GAIN

TEST SERIES NO.		C2	C0
Proportion (%)	Granular A	70	70
	Pellet	25	25
	Fines	5	5
	$CaCl_2$	2	0
Strength (psi)	3 days	240	260
	7 days	675	1270
	14 days	1407	1530
	28 days	1900	1950

water content w = 10%

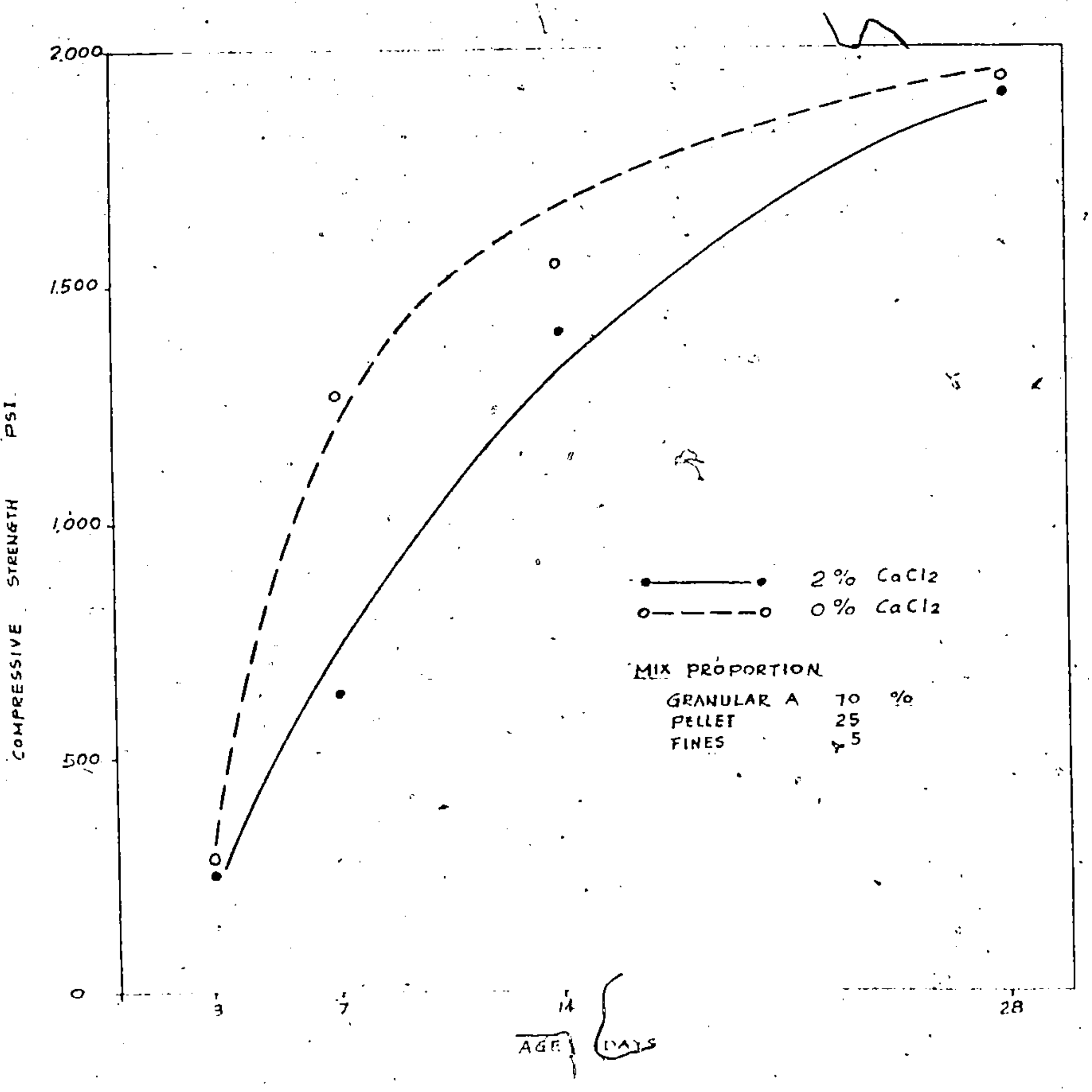


FIGURE 3-6 COMPRESSIVE STRENGTH vs CURING AGE FOR 2% $CaCl_2$ ADDITION

TABLE 3-18

GLASS CONTENT - FINENESS - STRENGTH

TEST SERIES NO.		21-5	21-10	GTT-2	GTT-5	GTT-10	2	5	10	G7	GB
Proportion (%)	Granular A	70	70	70	70	70	70	70	70	70	70
	Pellet	25	20	28	25	20	28	25	20	28	28
	Fines	5	10	2	5	10	2	5	10	2	2
Glass Content of Fines (%)		99		74			47			83	65
Blaine Fineness of Fines (cm^2/gr)		3542		2850			3430			...	...
Strength (psi)		820	1890	760	1340	2190	600	1270	2690	700	360

GTT, 2, 5, and 10 are given again for comparison purposes.
Fines used in GB are from Buffalo Slag.
Water content w = 10%.

slag related to the temperature which the granulated slag has experienced and chemical composition of the slag. Even with a high glass content, the Buffalo slag fines gave extremely low compressive strengths. To investigate possible reasons for this, an ultra-violet light test was conducted on the various slags used in this series. The Buffalo slag pellets showed a blue grey colour whereas the other pellets emitted a pink colour. Organizations such as CILAM consider a blue grey colour to indicate low activity and pink to indicate high activity [60]. This lack of "potential activity" may explain the very poor compressive strengths associated with Buffalo slag pellets.

It should be noted that pellets of glass contents higher than 80% are very friable and may exhibit high grindability. Some of the erratic nature of the test results could be due to this friable nature at higher glass contents. Fineness effects on strength gain are shown for test series Nos. 3 and 5 in Table 3-9. (The fineness has been determined throughout all the research with the standard Blaine air permeability equipment and is subject to the usual limitations on this method. However, as a standard method and equipment has been adopted, the fineness determination should be consistent and certainly suitable for comparison purpose.)

Strengths for No. 3 specimens containing ball mill fines (Blaine fineness of 2000 cm^2/gr) are much higher than those for No. 5 specimens containing natural fines (Blaine fineness of 1000 cm^2/gr), provided that all the other factors remain constant. Thus, the fineness effects shown in Table 3-18 may be superseded by many other factors and should not be viewed as indicative of fineness trends.

Step 5: Optimum Lime Content and Catalysis Effect of Portland Cement

Investigations of the optimum lime content (expecting the critical value to be in the range of 2% to 10% by weight of ground fines) and catalysis effect of portland cement on compressive strength gain, were conducted to determine if the addition of such "activators" would be of benefit. The optimum lime content was determined by using compressive strength specimens consisting of 70% granular A, 25% pellets and 5% total fines made up of various proportions of ground fines and lime. These proportions are shown in Table 3-19 with the respective compressive strengths. The results are also summarized in Figure 3-7.

Cube specimens were prepared to determine the catalysis effect of portland cement (type 10). These specimens consisted of ground fines, portland cement and Ottawa sand. Mix proportions and compressive strengths for each test series are given in Table 3-20 and Figure 3-8.

The lime and catalysis effects can be summarized as:

1. For the mixes examined, it was found that the optimum lime content was 5% by weight of total fines (ground fines plus lime) giving a compressive strength of 1380 psi. Unlike other siliceous materials, or portland cement, the ground pellets appear to contain approximately the amount of lime which is necessary to produce the cementitious gel of tobermorite associated with the silica. It should be noted that this

TABLE 3-19

OPTIMUM LIME CONTENT

TEST SERIES	GROUND FINES AND LIME PROPORTIONS							STRENGTH (b)(c) (psi)
	GROUND -#200 FINES		LIME ($Ca(OH)_2$) (a)			TOTAL		
	%	Weight (g)	%	Weight (g)	Wt of CaO	%	Weight (g)	
OP1	99	223	1	2	1.43	100	225	1120
OP3	97	218	3	7	5.01	100	225	1080
OP5	95	214	5	11	7.87	100	225	1380
OP10	90	203	10	22	15.73	100	225	1050
OP20	80	180	20	45	32.18	100	225	755
OP40	60	135	40	90	64.35	100	225	680

(a) Wt of CaO obtained from Wt of $Ca(OH)_2$ x 0.945 x 0.76, the purity of hydrated lime is 94.5%.

(b) Average for two specimens prepared by modified Proctor compaction, with 10% water content and 7 days curing at 100°F oven.

(c) Specimen mix proportion, Granular A 70%, pellet 25%, ground fines and lime 5%.

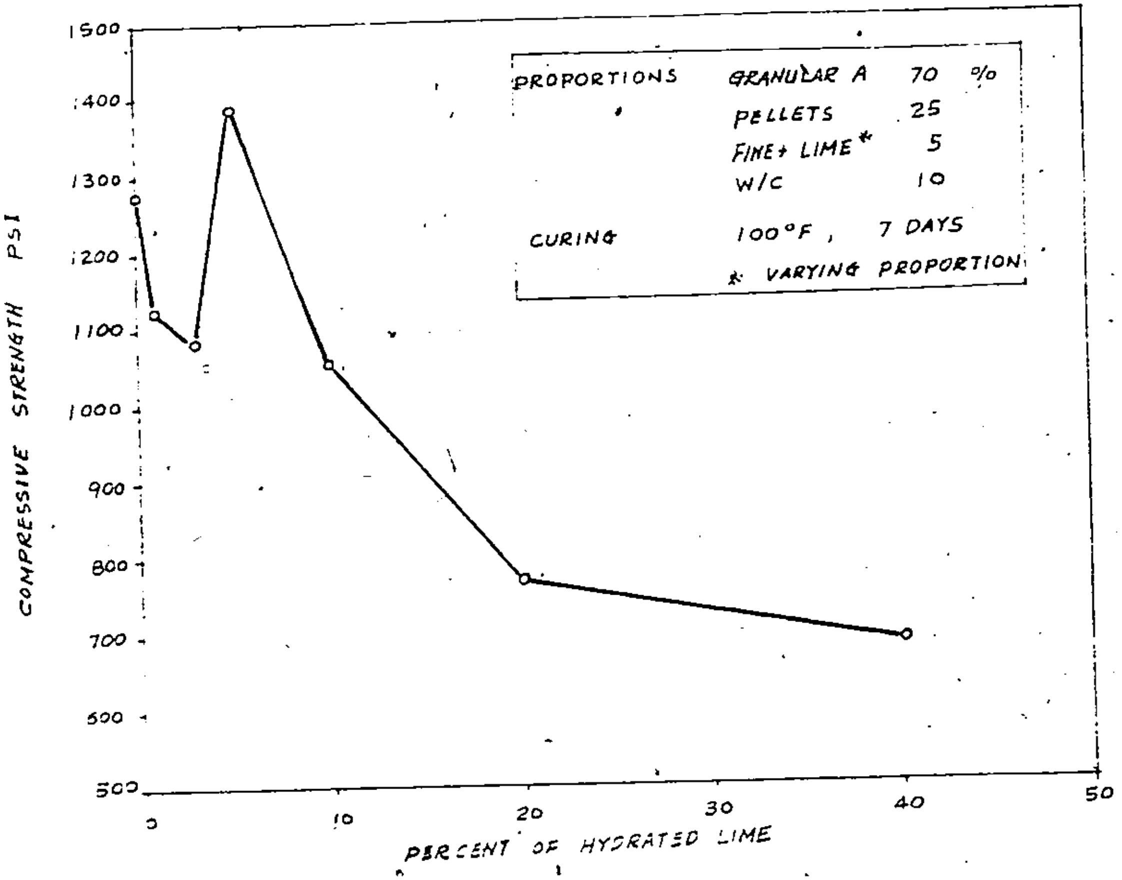


FIGURE 3-7 OPTIMUM LIME CONTENT FOR MIXES CONTAINING 5% OF -#200 GROUND PELLETS FINES (BALL MILL) AND LIME

TABLE 3-20

CATALYSIS EFFECT OF PORTLAND CEMENT

	TEST SERIES NO.		PC0	PC2	PC5	PC10	PC20	PC50	PC100
Proportion (%)	Ottawa Sand		73.3	73.3	73.3	73.3	73.3	73.3	73.3
	Fines + Portland Cement		26.7	26.7	26.7	26.7	26.7	26.7	26.7
		Fines	100	98	95	90	80	50	0
		Portland Cement	0	2	5	10	20	50	100
		Total	100	100	100	100	100	100	100
Strength	(psi)		670	470	440	560	910	1360	2420

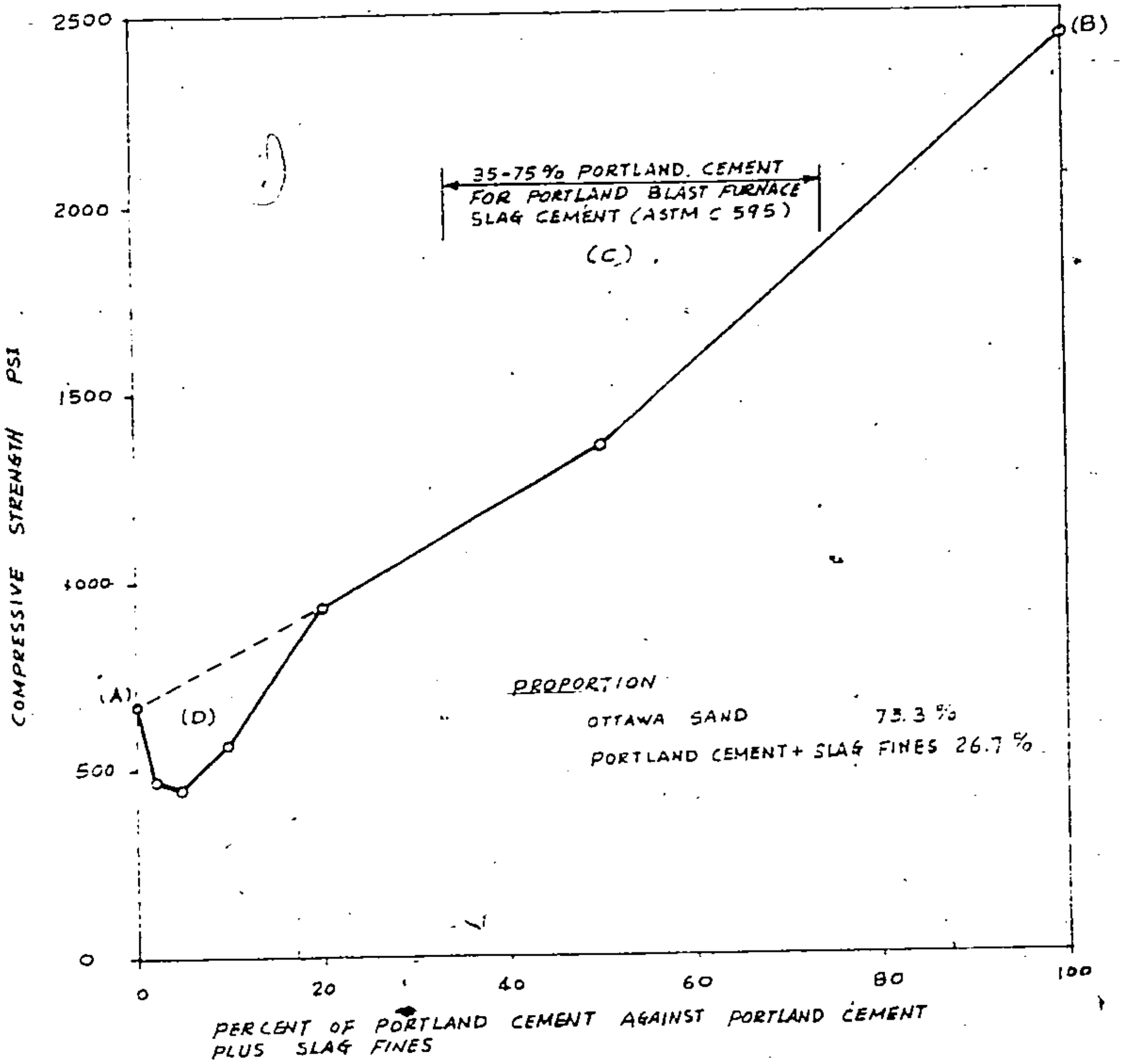


FIGURE 3-8 CATALYSIS EFFECT OF PORTLAND CEMENT ON SLAG FINES

optimum lime content determination was conducted using a specific aggregate combination and lime; along with given curing conditions such as temperature and times. If a different combination of aggregates and lime and/or other curing conditions were adopted for such an evaluation, the optimum lime content may shift. It is apparent that the addition of small amounts of lime may improve the strength while large amounts will significantly decrease the strength. This indicates that lime addition is probably not required. Some care should be adopted in determining the actual calcium oxide which is the effective component. The lime used was in the hydrated form, $Ca(OH)_2$, which has a molecular weight of 74 and purity of 94.5%. Therefore, the actual percent of calcium oxide (CaO) of molecular weight 56 in this hydrated lime is only 71.5% (56/74 x 94.5%). Thus, the effective CaO content at 5% hydrated lime by weight of total lime (ground fines plus lime) is reduced to 3.58%.

Another approach for determining the optimum lime content is a method based on detecting the unreacted free lime in the system through X-ray diffraction techniques [51]. Since stabilized base design is concerned with the strength of the final product, the former approach was considered sufficient in developing guidelines.

2. In general, the compressive strength of the cube specimens increased with greater portland cement content in the Ottawa

sand, ground pellets and portland cement mixes except for those mixes containing less than 5% portland cement. In Figure 3-8, point (A) means slag cement as defined by ASTM C595-74, point (B) portland cement, and zone (C) portland blast furnace slag cement, with regard to the composition. The depression of zone (D) on the curve may possibly be due to errors in specimen preparation and curing procedures, or not enough portland cement content to integrate or influence the catalysis effect. Also, it should be noted that other pellet fines under various curing conditions may result in different trends.

Step 6: Autoclaved Curing of Stabilized Base Specimens and Bricks

The strength gain of stabilized base specimens and typical building bricks which were made with various aggregates and pellet fines (LA fines) was accelerated by autoclave curing at Ontario Building Supplies Limited, who co-operated in this particular study. Three specimens for stabilized base, with 25% fines, were autoclaved and then tested for compressive strength in order to find the effect of autoclaving on strength gain. These test results and a typical autoclaving trace are shown in Table 3-21 and Figure 3-9. These special base stabilization specimens were cured at 100°F for two days before transportation in the still "green" state to Toronto for autoclaving. Three sets of brick of standard size, 4 in. x 2 1/2 in. x 8 1/2 in., were autoclaved and tested for compressive strength, modulus of rupture and absorption. These test results are shown in Table 3-22. The bricks

TABLE 3-21

STRENGTH OF AUTOCLAVED SPECIMENS

NO. OF TEST SERIES		A1	A2
Proportion (%)	Granular A	70	70
	Pellets	5	5
	Fines (a)	25	25
Water Content (%)		8.9	8.9
Curing		2 days in 100°F oven then autoclaved 3.25 hours to pressure of 130 psi (347°F) 15 hours at 130°F 2 hours blowdown	2 days in 100°F oven then autoclaved 5.5 hours to pressure of 100 psi (327°F) 14.5 hours at 100°F with immediate blowdown
Strength (psi)		5460	5400
Remarks		average of two specimens	result of one specimen

(a) stone ball mill fine from pellets

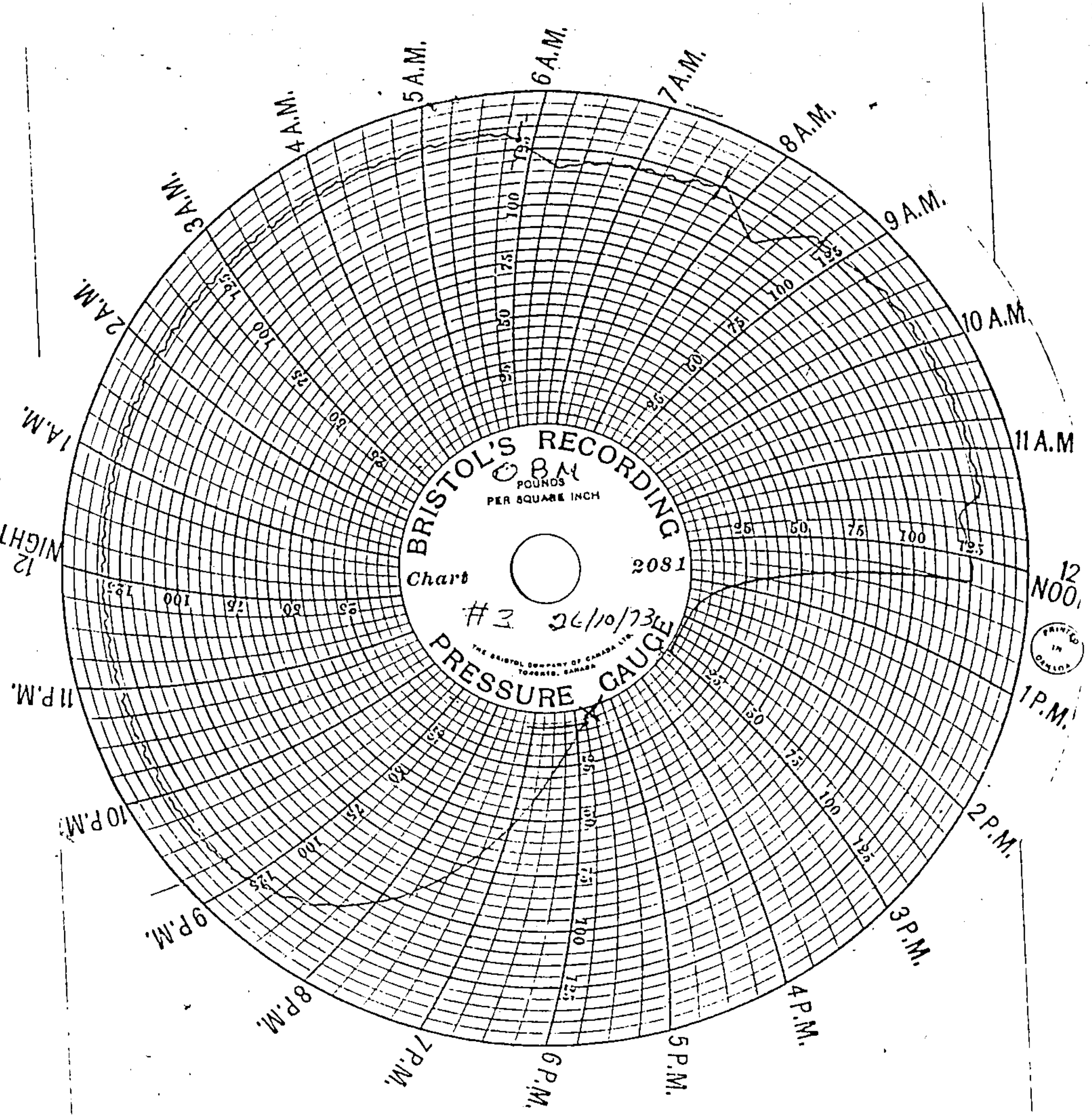


FIGURE 3-9 AUTOCLAVE PRESSURE GAUGE CHART INDICATES THE TEMPERATURES FOR EACH PRESSURE

TABLE 3-22

BRICK TESTS

NO. OF SET		B1	B2	B3	ASTM C55-55 CONCRETE BRICK
Composition (%)	Pellet	40	85	90	Mix of portland cement and suitable aggregates
	Fines	10	15	10	
	Fine Sand	25	...	...	
	Coarse Sand	25	...	...	
Unit Weight (pcf)		126	121	108	...
Bulk Specific Gravity		2.02	1.94	1.73	...
Modulus of Rupture (psi)		530	670	260	...
Compressive Strength (psi)		3620	5100	2330	Grade A-2500 psi, Grade B-1500 psi
Absorption (%)		13.4	11.1	14.8	15%

Fines made in stone ball mill from pellets.

One specimen for each test.

were autoclaved with 3 hours to a pressure of 130 psi ($347^{\circ}F$), 8.35 hours at 130 psi, 6.25 hours at 125 psi and then 3 hours blowdown.

The effect of the autoclaving was:

1. After a curing process of 2 days at 100°F and 20 hours in the autoclave, there was a strength increase of approximately 8% to 5,400 psi from the 5070 psi achieved with ordinary 7 days sealed curing at 100°F (see Test Series No. 25 in Table 3-13). This strength gain is not significant, however, autoclaving does offer the feature of quick curing of building products.
2. The autoclaved brick results are very promising with the ASTM specifications exceeded in each case. The modulus of rupture for the bricks is 11% to 14% of the compressive strength which is similar to the results observed for portland cement concrete. Bricks of higher unit weight show higher strength and lower absorption which are favourable features for building materials (comparing B2 with B3 which used the same aggregates and comparing B1 with B3 which used the same amount of fines). These results indicate the importance of gradation effects on density.

It is felt that ground pelletized slag has definite applications in the manufacture of high quality building bricks and that extensive research should be initiated on this topic. The savings in cement cost could be significant.

3-2 SLURRY SEALS

3-2-1 What is Slurry Seal?

Asphalt mixes consisting of bituminous binders and mineral aggregates can be placed in the form of a slurry with a workability similar to portland cement concrete and without any rolling. Two basic types of slurry are hot mix mastic asphalt concrete, or guss asphalt as it is called in Germany, and emulsified asphalt slurry seal or cold slurry. Guss asphalt is a mixture that consists of penetration grade asphalt, mineral aggregates and filler, and can be poured or cast in place requiring no rolling or compaction. Emulsified asphalt slurry consists of comparatively fine sharp aggregates, emulsified asphalt and water, that is mixed in a transit-mix truck to a free flowing consistency, and applied by the squeegee action of a spreader box.

Mastic asphalt concrete or guss asphalt is one of the main components of the pavement structure, helping to support the loadings imposed by vehicle traffic without plastic deformation while resisting abrasion and providing skid resistance [23]. In contrast, emulsified asphalt slurry seals are not generally applied to obtain structural capacity or high abrasion resistance, but to fill voids and cracks as a maintenance procedure that often improves skid resistance [23]. Asphalt cement binders hold the aggregate firmly on cooling in the case of mastic asphalt concrete and after evaporation of water or by chemical "break" for emulsified asphalt slurry seals. This thesis only deals with emulsified asphalt slurry seals.

3-2-2 - Purpose of Slurry Seals

As the name indicates, the prime function of a slurry is to seal the pavement surface, restoring "life" to hard, dry pavement surfaces, arresting ravelling and disintegration of old, worn surfaces, and developing or restoring safe, skid resistant surface texture. Seal methods other than slurry seal are: fog seal, which is a light application of bituminous materials; and, seal coat, which is a conventional asphalt and chip application. These two sealing methods are quite different from slurry seal in application of materials, and processes.

Slurry seal is mainly used for maintenance of roads as follows:

(a) as primes before heavier plant mix surfacings;

(b) as finish treatments on Macadam type surfaces or chip cover seals;

(c) to arrest scaling and deterioration of portland cement concrete pavements;

(d) to develop skid resistance on slick, fat, or polished surfaces;

(e) to renew dry, cracked, ravelling bituminous surfaces;

(f) as a retreatment prior to overlays;

(g) for sealing against the intrusion of water;

(h) to provide slight grade restoration with a minimum effect on curb height; and

(i) to provide a uniform appearance and texture.

Also, slurry seals can be applied for similar purposes to school playgrounds, parking lots, park driveways, pedestrian footpaths, airport runways and perimeter tracks.

The use of a slurry seal in a particular application is usually determined by the economics in comparison with other surface dressings and by traffic control considerations. The timing of application is another important factor in maintenance economy. Figure 3-10 shows the deterioration curve of a pavement surface for original and post slurry conditions. The crosses on this figure indicate the proper application of slurry to economize the overall pavement maintenance costs.

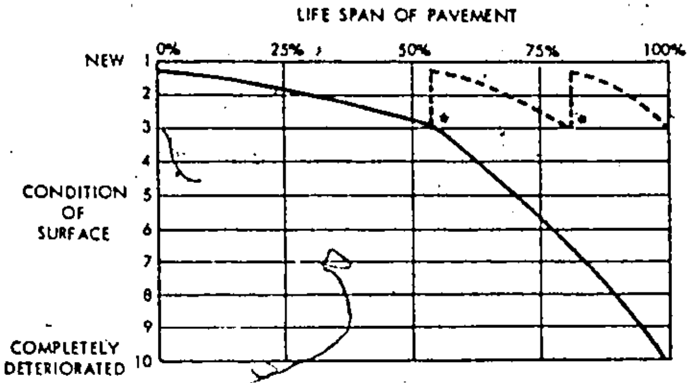
3-2-3 Types of Slurry Seals

Slurry seals can be categorized as anionic slurry seals or cationic slurry seals depending on the type of emulsified asphalt utilized in the particular slurry. These two types of slurry seals show a marked difference in their characteristics that must be clearly understood to take full advantage of their properties with varying aggregates and application conditions. Anionic slurry seals use anionic emulsified asphalts as their cementing agent and were first applied in the 1920's [96]. Cationic slurry seals employ cationic emulsified asphalts as their cementing agent and are a more recent development (1962) [96, 99] with first commercial applications in 1964 or 1965.

Depending on the number of courses in a particular slurry seal application, it can be classified as a single course or a multi-course slurry seal. Single course slurry seals have three basic types - fine, general, and coarse - according to the maximum size and gradation of aggregates used. In multi-course slurry seals, a thicker, coarser

EXPLANATION OF SURFACE CONDITIONS

1. Crack-free surface. Preventive maintenance will prolong life span
   Color: Black Texture: Smooth
2. Oxidation started. Short hairline cracks starting to develop.
   Color: Dark Gray
3. Loss of fines. Oxidation advanced. Hairline cracks are longer and wider.
   Color: Gray
4. Complete oxidation. Cracks are 1/4" wide and have base faults.
   Color: Light Gray
5. Moisture penetration. Texture of surface becoming rough.
6. Cracks widen. Shrinkage and cracking evident at curb and gutter lines.
7. Potholes develop. Gatoring cracks show up on soft spots.
8. Potholes enlarge. Gatoring areas begin to break up. Over-all texture very rough.
9. Heaving
10. General breakup of surface



ORIGINAL DETERIORATION CURVE ————————

POST SLURRY DETERIORATION CURVE - - - - - - - - - - - -

Points where preventive maintenance programs are most effective in reducing repair - replacement costs. *

FIGURE 3-10 DETERIORATION CURVE FOR A TYPICAL PAVEMENT SURFACE [97]

Graph shows how planned applications of slurry seal vastly improve life span of pavement. Cost of applications is substantially offset by repair - replacement savings.

slurry seal should normally be used under a finer surface slurry seal. However, over badly cracked surfaces, the finer slurry seal course can be applied first followed by a thicker course. The first course, and each course thereafter, may be opened to traffic before another course is applied.

Quick set (anionic or cationic) emulsified asphalts have been developed fairly recently that provide the solution to setting time problems which the previous slow set emulsified asphalts had been subjected to. These setting problems required great care to be taken with the weather, and the closing of pavements for substantial periods. Unfortunately, many aspects of quick set slurry seal construction are still in the developmental stages.

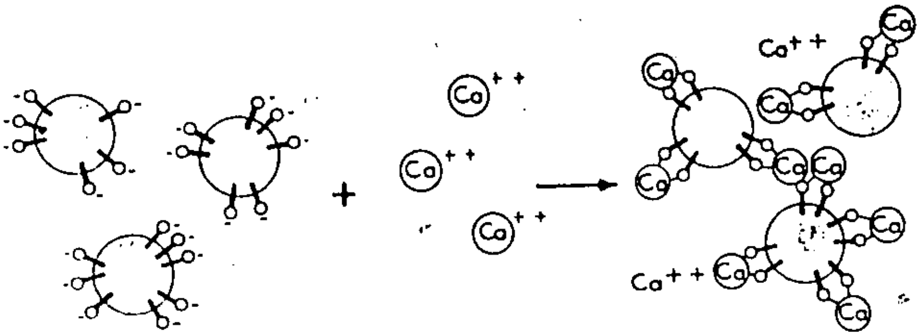
3-2-4 Mechanism of Slurry Seal Setting

The property of asphalt cements in the emulsified state that enables them to form an adherent coating on aggregates at relatively low temperature is the high pressure induced by the surface tension related to the infinitesimal radii of curvature of dispersed asphalt droplets. This high pressure lowers the temperature at which the asphalt flows and adheres to the aggregate particles. In a stable slurry which has a runny consistency, the asphalt remains emulsified at least during the mixing of slurry components. Nothing happens to the majority of the asphalt droplets until a process designated as the break (or set) of the emulsified asphalt begins. This break indicates that the runny slurry mix is beginning to set and will soon become hard.

On the electrically charged surface of emulsified asphalt droplets, the special emulsifiers in the asphalt react with the multi-valent aggregate surface or ions which are present. These ions may be released from hard water that contains calcium ions, lime, portland cement, steel slag, etc. Neutralization of the electrical charge allows the asphalt droplets to coalesce or break, and the neutralized asphalt droplets attach to the aggregate forming a lattice of asphalt cement which gives cohesive strength to the final asphalt cement-aggregate mix. Figure 3-11 shows this mechanism between anionic quick set emulsified asphalt droplets and cations released from the aggregate or mineral fillers. Figure 3-12 shows the corresponding reaction between aggregate and cationic emulsified asphalt.

The mechanism described above shows the initial chemical set of quick setting emulsions resulting in cohesive strength between asphalt and aggregate. Further strength can be developed due to the dehydration of the system. This dehydration is accelerated by higher temperatures and lower humidity as in the case of the slow setting types of emulsified asphalt in which attachment of the asphalt to the aggregate is accomplished primarily by evaporation of water. Figure 3-13 shows the cohesive strength due to initial set and dehydration. Although the final cohesive strength of both quick and slow set emulsified asphalts reaches the same valve, the initial early strength by quick break is the main concern in slurry seal construction.

It should be noted that the addition of portland cement or lime to the slow set type emulsified asphalt-aggregate system does not cause a quick set reaction. However, for specially developed and designed quick set emulsified asphalts, portland cement or lime is required to "trigger" the chemical setting mechanism. Without such mineral fillers (portland

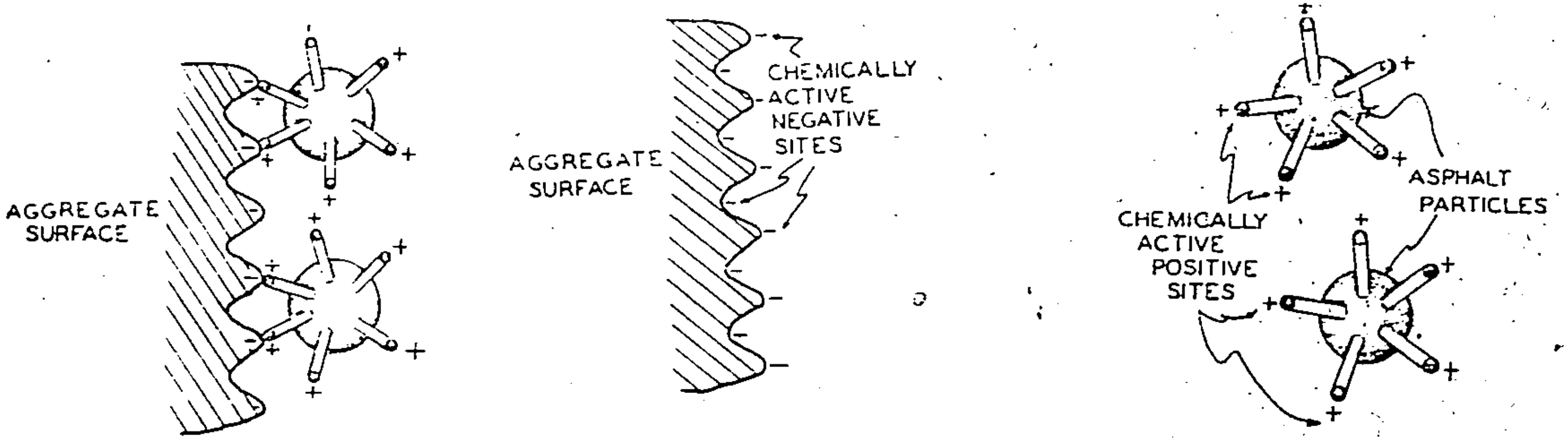


ANIONIC (NEGATIVELY CHARGED) EMULSIFIED ASPHALT

THE CEMENT OR LIME, FILLER RELEASES MULTIVALENT CATIONS (I.E. CA^{++})WHICH REACT WITH THE SPECIAL QS EMULSIFIERS

AND THE EMULSIFIER IS RENDERED INACTIVE NEUTRAL ASPHALT PARTICLES. NOW ATTACH TO THE AGGREGATE AND COALESCE. THE SLURRY SEAL MIX IS NOW SET, HAS TENSILE STRENGTH AND IS UNAFFECTED BY WATER (RAIN RESISTANT)

FIGURE 3-11 SETTING MECHANISM OF ANIONIC QUICK SET SLURRY SEALS [30]



The reaction between an aggregate and emulsion neutralizes some of the electrical charges. This permits the emulsion particles to coalesce.

Assumed Illustration of an Aggregate Surface

Emulsified Asphalt Particles

FIGURE 3-12 SETTING MECHANISM OF CATIONIC QUICK SET SLURRY SEALS [30]

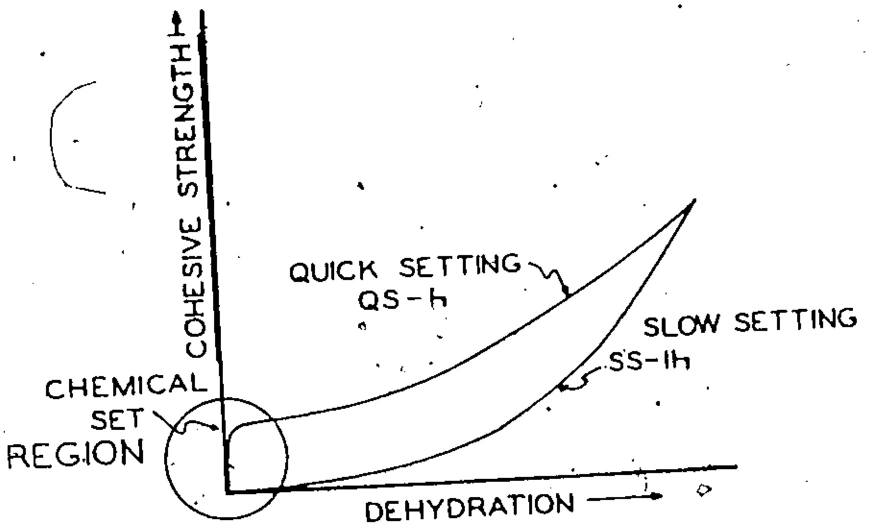


FIGURE 3-13 COHESIVE STRENGTH AS A FUNCTION OF DEHYDRATION FOR THE QUICK-SETTING AND SS-1h SYSTEMS [30]

cement or lime) , the quick set slurry mix will behave like a slow set emulsified asphalt slurry mix. Since steel slag contains free lime, it may be possible that one of these specially developed emulsions can be utilized in a steel slag slurry seal.

After slurry mixes start stiffening or breaking, continued mixing or overmixing produces an unacceptable distribution of asphalt on the aggregate. The bulk of the larger aggregate is left partially uncoated and thick films remain on the fines. When a quick set emulsified asphalt breaks, by mixing in an appropriate amount of additional water, a slurry can be formed containing coated, partially coated and uncoated particles, and solid or semi-solid particles of nearly pure asphalt. This mix is similar to a stable slurry formed by water-emulsifier-aggregate without asphalt cement. The longer mixing is undesirable and causes the after-break mixing or entraining of air into the system, and results in a puffy malt-like appearance. This slurry also loses its lustre and will often leave a discoloured spot on the pavement.

3-2-5 Mix Design Considerations for Slurry Seals

The two prime considerations in the mix design of slurry seals are the behaviour of the slurry during mixing and placing processes and the performance of the placed slurry seal under traffic action. Aggregates, emulsified asphalt, water, additives and environmental factors are of main importance to both design considerations, before and after placing the slurry seal. The first four factors can be controlled, but environmental factors (temperature, wind, humidity, etc.) , while avoidable, cannot be controlled.

3-2-5-1 Aggregates

Since aggregates generally occupy 87% to 94% of the finished product, the quality and gradation of aggregates has an important influence on the stability, breaking time and performance under traffic of the slurry seal. The type of aggregate used (electro-positive, such as limestone, or electro-negative, such as silica and quartz) determines the emulsion type selected to insure the proper reactivity between aggregate and emulsified asphalt. Generally, anionic emulsions are adopted with electro-positive aggregates and cationic with electro-negative. The maximum size of aggregate and gradation, as well as contained plastic fines like clays, are the most important considerations in application of slurry seals. The optimum amount of emulsified asphalt is largely dependent on the aggregate gradation which governs the specific surface and oil absorption. It is critical that each aggregate particle ends up with a uniform coating of asphalt cement.

ISSA (International Slurry Seal Association) specifications [100] for slurry seal aggregate gradations, as shown in Table 3-23, are typical of the gradations suggested by various organizations. Four types - fine seal (Type I), general seal (Type II), coarse surface (Type III), and base course (Type IV) - are included in the ISSA specification for aggregate gradations. Types I and II are mainly for surface course applications, Type III for the first and/or second courses of two-course applications and Type IV for base courses. The effect of aggregate gradation on the performance of a slurry seal is depicted in Figure 3-14.

A sand equivalent [40] of minimum 40 to 45 is recommended in order

TABLE 3-23
GUIDE GRADATIONS FOR SLURRY SEAL [100]

SIEVE SIZE	TYPE I FINE SEAL	TYPE II GENERAL SEAL	TYPE III COARSE SEAL	TYPE IV BASE COURSE
PERCENT PASSING				
1/2"	100	100	100	100
3/8"	100	100	100	80-90
#4	100	90-100	70-90	60-82
#8	90-100	65-90	45-70	40-60
#16	65-90	45-70	28-50	28-45
#30	40-60	30-50	19-34	19-34
#50	25-42	18-30	12-25	12-25
#100	15-30	10-21	7-18	8-17
#200	10-20	5-15	5-15	4-8
Asphalt cement required, percent of dry aggregate (Not including water portion)				
Asphalt cement	10-16	7.5-13.5	6.5-12	5.5-7.5

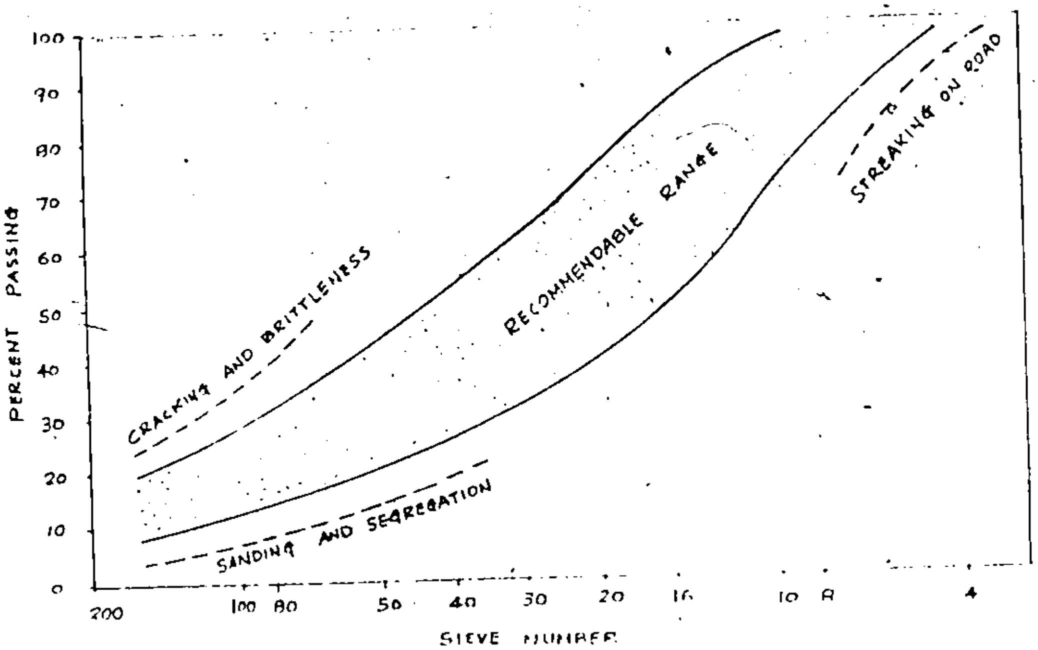


FIGURE 3-14 REGION OF GRADATION SUITABILITY FOR SLURRY SEAL

to detect any potential detrimental effects of clay like plastic fillers. Such fillers are not generally detected in the WTAT [24] (Wet track abrasion test) because the one hour soaking period utilized is not sufficient to cause swelling.

3-2-5-2 Emulsified Asphalts

The selection of emulsified asphalt - cationic or anionic, quick or slow set - depends on the choice of aggregate which is too often a simple economic consideration. Often, this choice of aggregate should also reflect the technical problems that can occur with some aggregates. There is no appreciable effect of asphalt penetration on wear in the range between 60/70 (SS-1h) and 200/300 (SS-1h) [40]. However, softer grades are often used in cooler weather and harder grades in warm weather. The optimum amount of asphalt (or emulsified asphalt) should be determined from the viewpoint of performance and overall cost. Excessive emulsified asphalt results in a slick, bleeding surface as well as wastefulness, whereas too little emulsified asphalt causes ravelling, sanding and lack of adhesion to existing pavements.

In order to avoid these problems, the theoretical asphalt content is estimated assuming that the optimum pavement performance is attained when each particle of aggregate is coated with asphalt cement to a thickness of 8 to 9 microns. With this assumption, the optimum asphalt content is determined by the area method [40] or California method [40]. The required asphalt content is the amount necessary for absorption into the aggregate surface, plus the amount to coat all the particles to the desired thickness [26]. If necessary, in addition to the amount of asphalt required by the above two methods, extra asphalt to fill any pores in the underlying road surface should be applied.

The wet track abrasion test has been developed for evaluation of quantitative wear values, defined as grams wear per square foot of abraded area, to determine if a slurry seal design will be suitable under simulated field conditions. Correlation of WTAT results with field performance has been investigated for 100 slurry seal projects, resulting in an acceptable wear value of 100 [40]. An increase in emulsified asphalt content generally decreases the wear value linearly as shown in Figure 3-15 [40].

3-2-5-3 Water

Water is used in the mix for two purposes: to develop a uniform dispersion of emulsified asphalt over aggregate surfaces, and, to insure consistency during application. In actual practice, the latter is the controlling factor. This water is supplied by three sources: water in the emulsified asphalt; moisture associated with the aggregate; and, prewet water if required. The total amount of water in the slurry from all sources affects the consistency. Excessive water results in segregation and rapid settlement of fine aggregate particles in the slurry, whereas too little water causes balling and coagulation and the slurry becomes too thick to handle and place. The greater the water content, the longer the period required for the emulsified asphalt to break and for the asphalt to attach itself to the aggregate. For a given aggregate [27], more total water is required with a cationic than with an anionic emulsified asphalt.

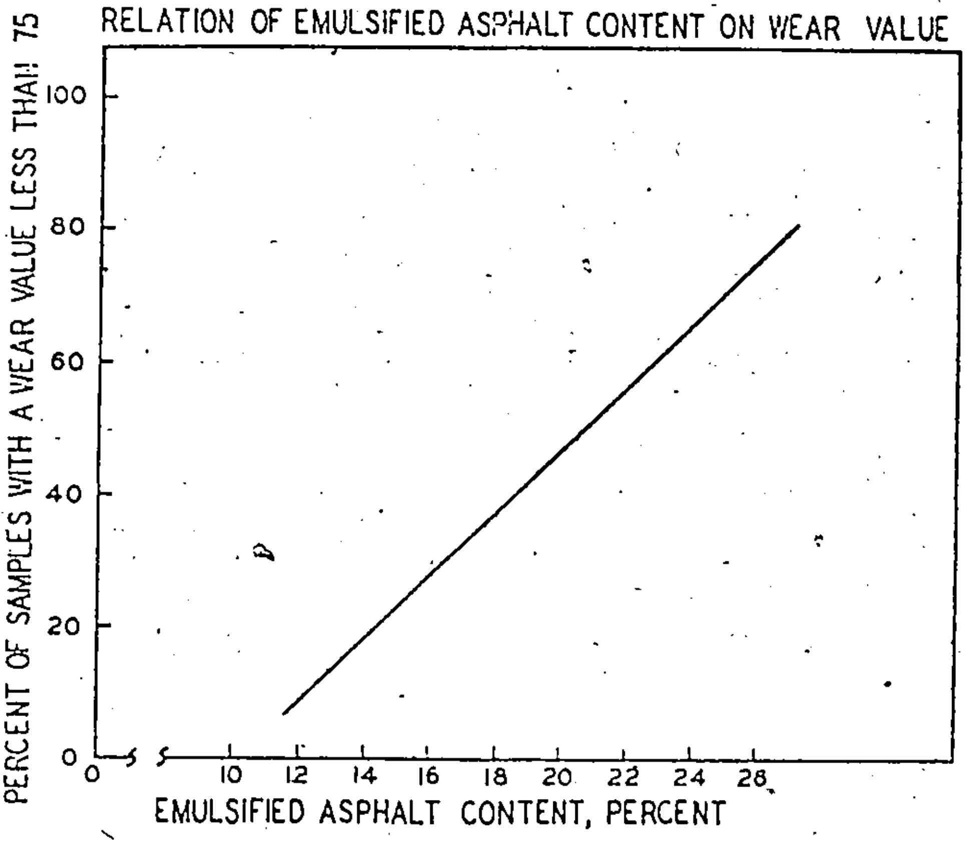


FIGURE 3-15 EFFECT OF EMULSIFIED ASPHALT CONTENT ON WEAR [40]

As indicated above, the function of water in slurry seal mixes is essentially to control the viscosity of the slurry, but water itself does not affect mixing stability. A method for determining the optimum water content for proper consistency has been suggested by Young [92] (Young consistency test). The stick test [26, 27], is another simple method that can be conveniently applied in the field to check the consistency and stability of slurry mixes.

3-2-5-4 Additives and Fillers

When mineral fines, usually passing the #200 sieve (fly ash, portland cement, powdered limestone dust), are used for improving the gradation, and they do not effect setting or stability, they can be considered as fillers. When such fines are used to modify the stability, acceleration or decceleration of setting or breaking time, they are considered to be additives. Chemicals such as Redicote E-11 [96] and acid chemicals for mixing aids [59] are common additives. Depending on their function, lime and portland cement can be fillers, additives or a combination. Thus, often there is no demarkation line between a processing aid (additive) and a gradation modifier (filler).

With some combinations of acceptable emulsified asphalt and aggregate in optimum proportions, no amount of added water will result in a stable mixture in which the heavier material remains in suspension. Mineral filler, notably portland cement, often overcomes this deficiency. This modification is essentially due to the higher density of a liquid mix of filler (portland cement) and emulsified asphalt, analogous to the use of bentonite muds to support open excavations.

3-2-5-5 Environmental Effects

Uncontrollable environmental effects such as temperature, relative humidity and wind velocity have an important influence on the placing and curing rate of slurry seals. In hot weather, the mix will set quickly because of accelerated chemical setting and rapid dehydration. Higher wind velocity and lower relative humidity also accelerate the dehydration resulting in quicker curing. Since rain can ruin a slurry that has not set, it is critical that applications have favourable conditions during the curing period.

3-2-6 Slurry Machines

Self-propelled slurry seal machines have been developed. Typically, these machines have equipment to perform two functions: slurry mixing which involves aggregate bins, aggregate gate and mixer; and, slurry spreading which involves a spreader box with rubber squeegee, slurry divertor and compartments. The auxiliary equipment includes an emulsion pump, fines feeder and water spray bar. Generally this equipment is all mounted on a truck and somewhat resembles a ready-mix truck. Equipment is also required to prepare a clean surface for application.

Water that evaporates from the slurry will leave an air voids content as high as 25% in the cured slurry. In usual practice, these voids are reduced under the action of traffic compaction. If traffic compaction is not anticipated, rolling can be used to reduce the voids. A relatively low voids content is necessary to minimize water penetration and weathering. As slurry seals are becoming more common, and require a finer aggregate gradation, this may be an excellent usage for steel slag.

3-2-7 Details of Materials Used for the Steel Slag Slurry Seal Development Research

Steel Slags, emulsified asphalts and pickle liquor, which were described in general earlier, were used to investigate the high lime content problems involved in developing steel slag slurry seals. The pickle liquor was used primarily in attempts to "neutralize" the steel slag.

3-2-7-1 Steel Slags

Steel slags supplied by STELCO and DOFASCO have high free lime contents that are typical of most steel slags. Two types of STELCO steel slag, from open hearth (OH) and basic oxygen furnaces (BOF), were analysed by the STELCO Research Centre for chemical composition. These chemical compositions are given in Table 3-24. Typical gradations of steel slags are given in Table 3-25. It should be noted that there will be day-to-day and even batch-to-batch variations in gradation and chemical composition of steel slags according to the specific process and product involved. A bulk specific gravity of approximately 3.3 and PH of 10 to 11 is typical for these steel slags.

3-2-7-2 Steel Pickle Liquor

Spent sulphuric acid pickle liquor from the hot strip mill and zinc sheet mill supplied by STELCO were used as received. A chemical analysis of pickle liquor from the zinc sheet mill determined by STELCO

TABLE 3-24

CHEMICAL COMPOSITION OF STEEL SLAG [23]

(BY STELCO)

CONSTITUENTS		PERCENT	
		OH	BOF
Calcium Oxide	CaO	25.8	41.3
Silicon Oxide	SiO_2	16.4	15.6
Aluminium Oxide	Al_2O_3	2.4	2.2
Magnesium Oxide	MgO	10.0	6.9
Iron	FeO, Fe_2O_3	26.0	20.0
Sulphur	S	...	...
Manganese Oxide	MnO	11.2	8.9
Titanium DiOxide	TiO_2	0.8	0.5
Free Lime	Free CaO	2.1	3.3

TABLE 3-25

GRADATION OF STEEL SLAG [23]

SIEVE SIZE	PERCENT PASSING	
	FROM STELCO*	FROM DOFASCO
3/4"	100.0	100.0
1/2"	99.9	100.0
3/8"	95.1	96.3
#4	64.3	60.0
#8	34.8	35.8
#16	18.3	21.6
#30	10.5	13.6
#50	7.0	8.9
#100	3.9	5.3
#200	1.3	1.6

* Average for OH and BOF steel slags

showed the following composition: Free H_2SO_4 - 47.90 grams/liter; Total SO_4 - 94.70 gr/l; Total Fe - 0.80 gr/l; and, Zinc - 20.00 gr/l.

3-2-7-3 Emulsified Asphalts

Basic details on the emulsified asphalts used are given in Table 3-26. Both the supplier (Chevron Asphalt Company, Limited) and ASTM designations are given.

3-2-8 Test Methods

The various test methods used during this research on steel slag slurry seals are listed in Table 3-8.

3-2-9 Steel Slag Slurry Seal Testing Schedule

Steel slag containing a fair amount of free lime and with a PH of 10 was investigated for potential slurry seal design using QS-h, QS-Kh and SS-lh emulsified asphalts or blends of these emulsions. The gradation of the steel slag was controlled by sieving out oversized material. The sand equivalent was determined for this controlled gradation. Optimum asphalt contents were calculated using the area method and California Highway Department Method. Finally, Young consistency tests and wet track abrasion tests were conducted on the various steel slag slurry seal mixes. A summary of the slurry seal test program is given in Table 3-27.

TABLE 3-26

EMULSIFIED ASPHALTS

TYPE OF EMULSIFIED ASPHALT			SUPPLIER	AC CONTENT (%)	PENETRATION OF RESIDUE
CHEVRON	ASTM	DESCRIPTION			
DM-h	SS-1h	Slow setting anionic (hard grade)	Chevron Asphalt Co.	42.0	95
QS-h	None	Quick setting anionic (hard grade)		65.5	94
QS-Kh	None	Quick setting cationic (hard grade)		60.0	114

TABLE 3-27

STEEL SLAG SLURRY SEAL DESIGN PROGRAM

STEP	PURPOSE OF TEST
1	(a) Steel slag and cationic quick set emulsified asphalt (QS-Kh) slurry seal examined for setting problem (b) Neutralization of steel slag with pickle liquor in attempt to reduce the high free lime content problem in slurry seal mixes.
2	(a) Steel slag, anionic quick set (QS-h) and anionic slow set (SS-1h) emulsified asphalts used in slurry seal mixes. (b) Blends of anionic quick set (QS-h) with anionic slow set (SS-1h) emulsified asphalts used in slurry seal mixes.

3-2-10 Test Results and Discussions

Step 1: Setting Problems and Neutralization with Pickle Liquor

DOFASCO basic oxygen furnace steel slag (BOF slag) and cationic quick set emulsified asphalt (QS-Kh) were used to form a slurry seal. The original gradation of steel slag with 34.4% retained on the #4 sieve was too coarse to meet the gradation requirements of a Type I slurry seal. All material retained on the #4 sieve was removed to obtain a gradation reasonably close to the Type I specification. This gradation is given in Table 3-28. Further changes were not made to the gradation since these would be difficult to perform in practice. It was found that the sand equivalent of this controlled gradation steel slag was 77, which is much higher than the minimum requirement of 45.

The theoretical asphalt contents were calculated using the area method and California method. For the gradation used, the measured value of specific surface area (SA) was 43.0 ft^2/lb, the apparent specific gravity (ASG) was 3.4 and the Centrifuge Kerosene Equivalent (K) was 4.85%.

(a) Theoretical Asphalt Content by Area Method

Total asphalt content (%) equals the amount required to coat all of the aggregate particle plus any asphalt absorbed by the aggregate:

$$= SA \times \frac{2.65}{ASG} \times 2.67 \times 10^{-3} \times 62.5 + K$$

$$= 43.0 \times \frac{2.65}{3.4} \times 2.67 \times 10^{-3} \times 62.5 + 4.85 = \underline{\underline{10.4\%}}$$

TABLE 3-28

CONTROLLED GRADATION OF STEEL SLAG

SIEVE SIZE	% PASSING	SPECIFIC SURFACE	
		SP. SURF. FACTOR	SURFACE AREA
3/8"	100.0	...	2.0
#4	100.0	2	2.0
#8	61.0	4	2.4
#16	38.2	8	3.1
#30	26.8	14	3.8
#50	20.2	30	6.1
#100	14.4	60	8.6
#200	9.4	160	15.0
TOTAL			43.0

(b) Theoretical Asphalt Content by California Method

(Test Method - California No. 355-A)

Total asphalt content (%) = 1.21 x K x ASG + 0.68

= 1.21 x 4.85 x 3.4 + 0.68 = 20.6%

The area method gives a significantly lower asphalt content than the California method. The optimum asphalt content is often found to be approximately the mean from these two methods - ≈ 15%.

Based on these theoretical values, a range of possible optimum asphalt contents from 12% to 20% were used to evaluate the wear value of steel slag slurry mixes. The amount of cationic quick setting emulsified asphalt corresponding to the required asphalt cement content (emulsified asphalts contain approximately 60% asphalt cement) was poured into the mixing bowl. Then a controlled amount of steel slag that had some pre-wet water in it was added and mixed, followed by additional water until a suitable consistency as determined by the Young Consistency Method, was achieved. Finally, WTAT specimens were prepared and tested to simulate the abrasion effects of traffic. These wear values indicate the expected performance of the slurry seal design in the field. The test results for this preliminary study are shown in Table 3-29.

It is normally expected that as the asphalt content is increased, up to a rich mix, that the WTAT wear will decrease. However, the test results turned out to be in reversed order of wear values. These reversed results were all caused by a unsatisfactory setting of the slurry and the different curing conditions. The lower wear values of Sets 3, 4 and 5 as compared to Sets 1 and 2 were caused by having to use higher curing temperatures. Sets 1 and 2, cured with the normal procedure

TABLE 3-29

SLURRY SEAL TEST RESULTS WITH STEEL SLAG (DOFASCO-BOF) AND QS-Kh

MIX NUMBER		1	2	3	4	5	REMARKS
Asphalt Cement Content	(%)	20	18	16	14	12	...
Emulsified Asphalt	(%)	33.3	30.0	26.6	23.3	20.0	60% AC
Total Water Content	(%)	15.0	15.1	13.8	14.0	14.1	water in E.A.+ prewet
Young Consistency Flow	(in.)	3.75	3.75	4.25	5	5	max flow 6.5
Wear Value	(gr/ft^2)	210	204	53	6	19	...

of 140°F for 15 hours, show higher wear values than the maximum of 75 usually specified. It can be assumed from this, and some previous field trials, that these unsatisfactory results are due to ~~the~~ high Ca^{++} ion content which is released from the free lime in steel slag. The Ca^{++} ions prevent the cationic emulsified asphalt from neutralizing the electric charge on the aggregate. As a result, the asphalt droplets are unable to coalesce or break and do not attach to the aggregate to develop the required cohesive strength. However, these mixes do give good workability and consistency during mixing and preparing the specimens as indicated by the Young consistency test results. What is required is a slurry seal design that will maintain this consistency and still break and cure properly.

From sets 1,2 and 3 it is apparent that an elevated curing temperature (15 hours at 230°F) can accelerate the setting and improve the unsatisfactory mixes through complete evaporation of water in the mix. While this prevents the adverse activity of Ca^{++} ions in the slurry seal mix, these favourable conditions cannot be expected in the field. In order to solve this setting problem, the alternative use of anionic emulsified asphalts was adopted for further tests.

In an attempt to control the PH value of the steel slag - cationic emulsified asphalt-water-system, steel pickle liquor containing about 5% free H_2SO_4 was added at the rate of 2% by weight to the mix. This acid pickle liquor caused severe bubbling in the slurry mix due to chemical reactions between the free lime and pickle liquor. The resulting slurry seal, when cured, still proved to be unsatisfactory. It was also felt that acids might cause corrosion problems with the expensive slurry seal equipment.

To decrease the free lime problem with steel slag as a slurry seal aggregate, washing with water was also tried. Each 300 grams of BOF or OH steel slag was subjected to 17 cycles of washing with water. The initial 200 cc of water was replaced by 150 cc of fresh water after each 24 hours of immersion and the PH was monitored 2 to 3 hours later and just before the next cycle. It was found that the original PH of 10.5 was not reduced after 17 cycles of this washing operation. It is doubtful that further washing cycles would eliminate the Ca^{++} ions. It is possible that larger volumes of wash water may have worked. However, these methods are not practical from an applications viewpoint. The simpliest approach would be to change one of the constituents, and since steel slag was a fixed ingredient, only the emulsified asphalt offered flexibility.

Step 2: Tests with Anionic Emulsified Asphalts

Anionic quick set (QS-h) and slow set (SS-1h) emulsified asphalts were next used in the steel slag slurry seal mixes. A new, coarse gradation of steel slag close to Type III was used as shown in Table 3-30.

The optimum asphalt cement content for this gradation was calculated to be 11% and 18% by the area and California methods, respectively. These results were based on a specific surface area (SA) of 52.8 ft^2/lb, apparent specific gravity (ASG) of 3.4 and CKE (K) of 4.3%. Mixes were prepared for asphalt cement contents of 8, 12, 16 and 20% using the anionic quick set emulsion (QS-h). The breaking of this special anionic quick set emulsion is triggered by lime and/or portland cement (i.e.

TABLE 3-30

GRADATION OF STEEL SLAG (DOFASCO-BOF)

SIEVE SIZE	PERCENT PASSING		SPECIFIC SURFACE	
	ORIGINAL GRADATION	CONTROLLED GRADATION	SPECIFIC SURFACE FACTOR	SURFACE AREA
1/2"	100.0	100.0	...	2.0
3/8"	96.7	100.0	...	
#4	79.1	90.0	2	1.8
#8	42.8	72.5	4	2.9
#16	23.4	60.0	8	4.8
#30	16.2	41.6	14	5.8
#50	10.9	28.0	30	8.4
#100	6.2	16.0	60	9.6
#200	2.8	7.2	160	17.5
TOTAL				52.8

Ca^{++} ions). All of these slurry seal mixes broke in 2 to 3 minutes, so quickly that preparation of specimens was not possible. As soon as mixing was stopped, the slurry began to stiffen, and remixing was prevented.

These test series indicated that measures were necessary to retard the setting or breaking of QS-h with steel slag. One possible method would be mixing QS-h with SS-1h to moderate or proportion the breaking time of these slurry mixes. Mixes were designed so that the combination of QS-h and SS-1h emulsified asphalt used resulted in 8, 10 and 14% AC in the final slurry seal after setting. The ratios of QS-h to SS-1h were 50/50, 30/70, 20/80, 10/90 and 0/100 (SS-1h alone) in order to control the setting time, since QS-h alone sets far too quickly in contact with the aggregate, while SS-1h shows the opposite trend. The steel slag used in these tests was found to be as follows: bulk specific gravity of 3.3 for coarse slag (+#4 sieve) and 2.9 for fine slag (-#4), apparent specific gravity of 3.6 for coarse slag (+#4) and 3.4 for fine slag (-#4); sand equivalent of 77 for fine slag (-#4); CKE averaging 4.2%; specific surface of 17.3 ft^2/lb (-3/8" sieve); and, optimum asphalt content of 6.5% and 12.9% by area method and California method, respectively.

The slurry mix test specimens were prepared and tested for slurry seal setting time (Chevron Test Method P-8), slurry seal setting test (Chevron Test Method P-11) and WTAT to evaluate the setting problems. These test results are summarized in Table 3-31, and Figure 3-16.

The best results were found to be for a 10% to 14% asphalt cement content with a QS-h/SS-1h ratio of 20/80. Lower asphalt cement contents

TABLE 3-31

SLURRY SEAL SETTING TEST

(A) SLURRY SEAL SETTING TIME TEST (TEST METHOD CHEVRON P-8)

No. of Mix	P8-10-20/80	P8-10-30/70	P8-10-50/50	P8-14-30/70	P8-14-50/50
QS-h/SS-1h Ratio	20/80	30/70	50/50	30/70	50/50
Final AC Content in Mix	10.2	10.3	10.2	14.2	13.8
Remarks	good slurry	good slurry	stiffened in 10 sec	good slurry	stiffened in 10 sec

DOFASCO steel slag passing 3/8" sieve

Test condition

Temperature 77°F

Loading Weight 400 grams

Loading time 5 secs

Specimen diameter 4.5"

depth 1"

TABLE 3-31 (Continued)

(B) SLURRY SEAL SETTING TEST (BROWN STAIN TEST CHEVRON P-11)

No. of Mix	P11-10-50/50	P11-10-30/70	P11-10-20/80	P11-10-10/90	P11-10-0/100	P11-14-50/50
QS-h/SS-1h Ratio	50/50	30/70	20/80	10/90	0/100	50/50
Final AC Content in Mix	9.8	10.0	10.0	9.8	10.0	14.7
Evaluation	set in 5 sec	set in 5 sec	passing	passing	passing (not complete)	passing start setting during specimen preparation

DOFASCO steel slag passing 3/8" sieve

(C) WET TRACK ABRASION TEST (WTAT)

No. of Mix	WT-8-30/70	WT-10-30/70	WT-14-30/70	WT-8-20/80	WT-10-20/80	WT-14-20/80
QS-h/SS-1h Ratio	30/70	30/70	30/70	20/80	20/80	20/80
Final AC Content in Mix	8.2	10.2	14.2	8.2	10.2	14.1
Wear Value (gr/ft^2)	not tested	not tested	not tested	83	38	35
Remarks	Stiffened too fast to prepare the WTAT specimens			good slurry few cracks on specimen surface passing P-11 Test	good slurry no cracks passing P-11 Test	good slurry no cracks passing P-11 Test

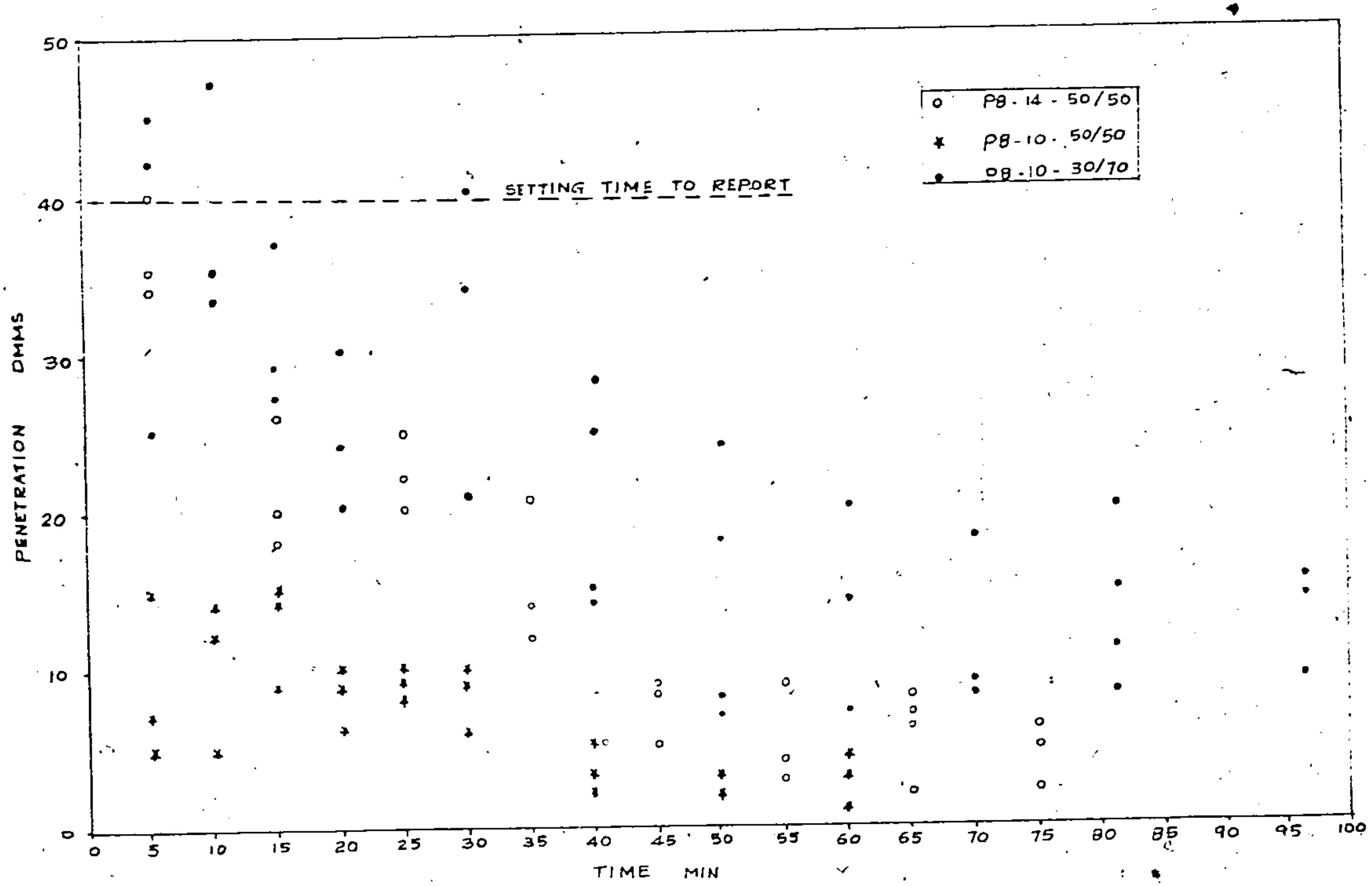


FIGURE 3-16 SLURRY SEAL SETTING TIME TEST (P-8 CHEVRON)

than 10%, which is the optimum asphalt cement content by average of area and California method, cause cracking due to a deficiency of binder, and a higher QS-h/SS1h ratio than 20/80 does not allow enough time for mixing and placing the slurry seal even for laboratory specimens.

It is believed that the -3/8" gradation gives a poor surface appearance (but high skid resistance) and most agencies would look for a -#4 design gradation. These preliminary results indicate that by proper blending of anionic emulsions, a satisfactory steel slag slurry seal can be designed. However, since the lime content is probably critical to the design, the inherent variability of steel slag composition will require a separate design for each type and supply of steel slag.

3-3 DATA BANK SYSTEM FOR WASTE UTILIZATION

As a backlog of information on waste utilization soon accumulated and continued to accumulate, it became necessary to develop a computerized waste utilization data bank system to store the essential details on each reference related to waste utilization for easy retrieval and analysis. This data bank is based on the keyword concept where the computer is used to store and locate references on the basis of certain keywords that best describe the information contained in the references. For this purpose, about 600 keywords were selected that were most suitable for describing waste utilization techniques from references in structures, transportation, geotechnical, general waste management and production, etc. These keywords were coded and sorted numerically and alphabetically. An importance factor indicating the significance of the reference, and a location factor indicating the availability of the reference (for example, the reference may also be from one of several abstracting services such as IRF, HRB, Institute for Scientific Information, etc.), are also used to increase the efficiency of the data bank. Some of the available information on waste utilization in construction was incorporated into the data bank and it is intended to continually up-date the data bank by monitoring the technical literature and subscribing to the pertinent abstracting services. Also, it is planned to make the waste utilization data bank available to other researchers and co-operate with other systems to avoid duplication.

This data bank system has been made a sub-set of a general Civil

Engineering Reference Program Utilization (CERPU) with the assistance of Mr. Paul Gripwell. Since CERPU works in either the batch or interactive mode, it can be used at other locations. The typical output format for a CERPU reference and one of the many CERPU references printed for a typical search involving base construction using slags are shown in Table 3-32. This CERPU search had the constraints that any reference must have the keyword "base course" and at least one other keyword from the group of "slag", "air-cooled slag" and "granulated slag".

While the preliminary work on CERPU was completed during this thesis research, the system soon grew to be an independent project. This system is still based on the general concepts developed above.

TABLE 3-32

COMPUTERIZED DATA BANK

```
        A.                   SAMPLE OUTPUT FORMAT FOR CERP
                        (Civil Engineering Reference Program)

NO. 0 --- SAMPLE ---

KEYWORD 1          KEYWORD 2          KEYWORD 3          KEYWORD 4          KEYWORD 5
KEYWORD 6          KEYWORD 7          IMPORTANCE         LOCATION           REFERENCE NUMBER

TITLE/  SAMPLE REFERENCE OUTPUT
AUTHOR(S)/        DOE J   SMITH J              JOURNAL/JOURNAL OR REPORT
VOLUME       NUMBER       DATE/DD MM YY                 CLASS OF ITEM

REMARKS
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           B.  TYPICAL CERPU REFERENCE FOR BASE CONSTRUCTION USING SLAG
                 (Civil Engineering Reference Program - Utilization)

NO. 6                                                                           NO. 6

AIR COOLED SLAG   GRANULATED SLAG   STEEL SLAG        ADVANTAGES         PAVEMENT
BASE COURSE       AGGREGATE         IMP/9             LOC/9              REF NUM/130

TITLE/  SLAG FOR ROADS - ITS PRODUCTION, PROPERTIES AND USES
AUTHOR(S)/        LEE A                         JOURNAL/J. INST HIGHWAY ENGINEERS
VOL/  16     NO/ 11       DATE/   11 68                  CLASS/ARTICLE

REMARKS/STATE-OF-THE-ART REPORT WITH EXTENSIVE REFERENCES AND DISCUSSION
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CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The research results can be summarized in three main areas:

1. A satisfactory base stabilization process utilizing ground pelletized blast furnace slag as the cementing material has been developed. Typical mix designs consisted of 70% air-cooled blast furnace slag (-3/4" crusher run granular A), (30-x)% pelletized slag and X% pelletized slag ground to -#200, with approximately 10% mixing water. The basic requirement of a developed compressive strength of at least 500 psi after 7 days sealed curing at 100°F was readily achieved for mixes containing relatively low percentages of -#200 ground pellets (for example, 600 psi when X equals 2%). Further tests indicated that higher compressive strengths are developed if all of the pelletized slag used in the mix (30%) is ground so that it contains the desired -#200 content. These higher compressive strengths are probably related to the creation of fresh, more "active" surfaces when the coarser pellets from the grinding are also utilized. It should be noted that none of these designs required the use of portland cement. A number of other aspects of pelletized slag base stabilization were considered such as energy utilization, catalysis effects of portland cement and lime, glass content of pellets, and fly ash utilization.

2. The setting problems associated with the high lime content of steel slags in emulsified asphalt slurry seals has been overcome. A blend of 20% quick set and 80% slow set anionic emulsified

asphalt resulted in a suitable slurry using a relatively coarse steel slag gradation (-3/8"). Attempts to neutralize the steel slag with spent pickle liquors or water washings were not successful.

3. A large amount of information on waste and secondary product utilization in highway constructions was accumulated and summarized during the research work. This information is given in tabular or summary form at pertinent locations throughout the thesis. A waste utilization data bank, CERPU, was initiated during this information retrieval aspect of the research and now forms a working system in the Highway Materials Laboratory.

It is believed that the detailed studies on pelletized slag stabilized base and steel slag slurry seal have indicated the largely undeveloped potential for waste and secondary product utilization in highway construction. The summary information on waste utilization that is integrated throughout should assist in developing future utilization studies.

4-2 RECOMMENDATIONS

Many of the research findings are of a preliminary nature and require additional confirmation and extension. Recommendation for future studies can be summarized under two main types:

1. Base stabilization utilizing ground pelletized blast furnace slag.
   (a) Methods for speeding-up the relatively slow strength development of slag-cement materials (catalysis agents, fineness, glass content, storage, handling, etc.).

(b) Practical grinding methods that do not require dry materials (optimum moisture content, type of grinder, handling, etc.).

(c) Utilization of natural aggregates and soils in the base stabilization.

(d) Correlations between strength development, glass content and pelletized slag chemistry and composition (including temperature effects).

(e) Critical evaluation of the freeze-thaw and wet-dry performance of stabilized base.

(f) Field applications and testing of the laboratory developed designs (including rate of curing).

Some of the above aspects have been considered, or are being considered, during extensions of the laboratory work to field applications sponsored in the Highway Materials Laboratory by National Slag Limited.

2. Emulsified asphalt slurry seal incorporating steel slags.

(a) Field applications of the laboratory based design (mixing, placing, setting, etc.).

(b) Consideration of other gradations and types of steel slags (finer gradations, open hearth steel slag, etc.).

(c) Production of blended anionic emulsions suitable for specific steel slag lime contents.

The assistance of slurry seal companies will be required with many of these studies.

Obviously, the waste utilization data bank, CERPU, must be maintained and kept current. Hopefully, CERPU will be made available to other researchers.

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APPENDIX 2-1

Ultra-Violet Test Method [60]

An ultra-violet test method has been developed by the German Research Institute under the assumption that there exist various kinds of glass with different hydraulic characteristics. In order to separate the different types of particles, the slag particles are exposed to ultra-violet light to luminesce.

It was indicated that particles which have pink radiation colours develop the highest strengths; yellow, grey-brown and blue radiation colours indicate lower strength; and, grains which include crystalline material and show blue and violet colours develop little strength.

APPENDIX 2-2

Procedure for Determining Glass Content

Microscope

While an Olympus Trinocular Model ECE Tr-1 microscope has been used, any microscope with the general polarizing features indicated below will be suitable. This microscope is equipped with a Model LSE high power interchangeable illuminator with transformer, eyepiece of P010X (polarizing), and objectives of 4X, 10X, 40X, and 100X. This allows magnifications of 40X, 100X, 400X and 1000X which is more than adequate for glass content determinations. The lower polarizing element is carefully adjusted to insure cross-polarization can be achieved, and the eyepiece can be adjusted quickly from plane to cross-polarized light.

Preparation of Slide Specimens

Representative samples are mixed and quartered down to about 15 to 20 grams, and the whole of this amount is then ground to various sizes such as #100 to #200 (passing through #100 sieve and retained on #200 sieve), #200 to #300 and #300 to #400 for each sample.

A very small amount of the desired size is then sprinkled on a microscope slide. A drop of Ethylene Glycol ($HOCH_2CH_2OH$) is applied to the centre portion of the sprinkled sample. A cover plate is then placed on top of the sample. The Ethylene Glycol then spreads below the cover plate by capillary attraction. After this occurs, the cover plate is sheared gently to form a uniform, single layer of particles (care must be taken to avoid air bubbles forming). Prepared slides should be labelled and handled carefully.

Examination of Specimens

The prepared specimen slide is mounted on the stage of the microscope, which has fine vernier horizontal movement controls. This mounted specimen is then examined under plane and cross-polarized light. Amorphous glass does not transmit cross-polarized light, but crystalline glass does and tends to grow. The determination of glass content is based on the average of 2 or 3 counts of 40 individual particles which appear at the cross-hair as the specimen is moved along one axis by the horizontal vernier. The glass content of individual particles is estimated to the nearest 10% by checking each particle (if necessary) under plane and cross-polarized light. The slide is moved from one end of the cover to the other end along one line, until an adequate number of particles are counted.

This general method of amorphous glass content determination follows that in the Particle Atlas [50].

Application of Method

The eyepiece of P010X was combined with the appropriate objectives according to the sample particle sizes to get the optimum condition for glass content determination:

Particle Size	Objective	Magnification
#50 to #100	10X	100X
#100 to #200		
#200 to #300	40X	400X
#300 to #400		
-#400	100X	1000X

However, particle sizes of #50 to #100 down to -#400 were used to find the effect of particle size on glass content. The examination of -#400 particle size is so fine that even under 1000X magnification it is difficult to estimate the glass content of each particle. A particle size of #200 to #300 is mainly used under 400X magnification because this size and magnification gives a reliable clear count for each particle.

APPENDIX 2-3

Equivalent Heat Table

FUEL	EQUIVALENT HEAT IN Btu	REFERENCES	USED IN THIS PAPER	UNIT COST
coal	10,000 per pound	[70]	13,000 Btu/lb	$13-18/ton
	10,000-15,000 "	[74]		
	14,022 "	[22]		
	13,469 "	[10]		
oil	144,000 per gallon	[70]	144,000 Btu/gl.	-
natural gas	900 per cu ft.	[70]	900 Btu/cu ft.	-
pelletized fuel made from garbage and solid waste	7,000-7,500 per pound	[74]	-	$3-5/ton
municipal waste	6,000 "	[74]	-	-

Conversion Table

FROM	TO	MULTIPLY BY
Kilograms	Pounds	2.204622
Metric tons	Short tons	1.10231
Metric tons	Long tons	0.98421
Metric tons	Barrels (376 lb)	5.8633 (cement)
Long ton	Barrels (")	5.9570 (")
Short ton	Barrels (")	5.3191 (")
Kilowatts	Horsepower	1.34102
Horsepower	Kilowatts	0.746
Btu (per second)	Horsepower	1.41460
Kilowatt hour	Btu	3413.44
Horsepower hour	Btu	2545.00

APPENDIX 2-4

Cost of Manufacture of Slag Cement

Description		Cost ($) per barrel	Remarks
Mill force, labour, superintendence		1.890	
coal 125 tons	10-12 $/ton	0.300	
lime 48 tons	24 $/ton	0.230	
slag 900 tons	3.75 $/ton	0.675	
repair		0.160	
oil and grease		0.080	
contingencies		0.065	
Total		3.400	18 $/ton

Note: Data from Maryland Cement Company, which has the production capacity of 5,000 barrel/month [22].

Costs for each item are adjusted from the original total cost of 0.35 $/barrel (1.88 $/ton).

Energy Requirements for Slag-Cement Manufacture

Dry process

1. Slag drying data at 500°C for removal of firmly bound water (refer to Table 2-24) indicates 9% by weight coke is required. However, of this, only about 10% is actually required for evaporation of the free water prior to grinding. Therefore, for one barrel, energy required is:

   376 lb x 9% x 10% = 3.38 lb of coke
   3.38 lb x 13,000 Btu/lb = 43,900 Btu/barrel.

2. Grinding to Fineness 76 mesh (82-92% passing)

450 to 800 Kg/hr using 25-30 Hp requirement [22]

2.66 to 4.65 barrel → 61,800 to 76,300 Btu 19,000 Btu/barrel

3. Total 43,900 + 19,000 = 62,900 Btu/barrel

<u>Wet Process [18] p 48</u>

1. Grinding 55 Kwh per ton = 10.3 Kwh per barrel

= 35,000 Btu/barrel