REGENERATION OF LANTHANUM FOLLOWING PRECIPITATION OF PHOSPHATES FROM WASTE-WATERS

REGENERATION OF LANTHANUM FOLLOWING PRECIPITATION OF PHOSPHATES FROM WASTE-WATERS

by

MARK WASSERLAUF, B.Eng.

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AUTHOR: Mark Wasserlauf, B.Eng. (McGill University)

SUPERVISOR: Dr. J. D. Norman

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ABSTRACT

Government programs now underway in Ontario aim at removing phosphates from waste-waters at sewage treatment plants. At present, removal of phosphates is commonly accomplished by chemical precipitation with lime, alum, or iron. Lanthanum, a rare earth element, has been found to be an effective precipitant of phosphates. If lanthanum precipitate can be collected, and the lanthanum then regenerated so that it could be recycled for further phosphate precipitation, a very advantageous alternative to the above schemes would result.

In this study, phosphates were precipitated from both distilled water and secondary effluent using lanthanum. For the two cases, a regeneration scheme for lanthanum was examined. The basic regeneration reactions were carried out to evaluate the kinetics and equilibria for different ratios of reactants and different reaction temperatures. Techniques for phase separation of reacted reagents were studied. Process design calculations were carried out to obtain order of magnitude figures for amounts and costs of chemicals required, amounts of sludge produced, and reactor sizes.

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TABLE OF CONTENTS

PAGE NO.

LIST OF FIGURES

PAGE NO.

LIST OF TABLES

PAGE NO.

PAGE NO.

CHAPTER I

INTRODUCTION

In recent years there has been increasing public awareness of deterioration of waterways due to accelerated growth of nuisance aquatic plant life. To halt this deterioration, government regulatory agencies are advocating control of the entry of such plant nutrients as phosphates and nitrogen into these waterways.

Programmes are now underway in Ontario which aim at removing phosphates in sewage treatment plants. Although methods for phosphate removal from waste-waters have been known since the 1930's, it is only recently that they have begun to be used to any significant extent. Of the various phosphate removal methods, the ones which appear to be most effective are those which rely on chemical precipitation of the PO_4 ion. The chemicals most often used today for this purpose are: alum, lime, and iron.

Recently work done by North American Rockwell scientists has shown that the rare earth element lanthanum can be much more effective than any of the above-mentioned reagents. The dosage required for phosphate precipitation with lanthanum is much smaller, and lanthanum is most effective at the pH levels of most waste-waters, thus eliminating the need for costly pH adjustment.

At present, lanthanum costs are at least 20 times as high as those of the chemicals used now, and thus, for it to become economically acceptable, a regeneration process which can reduce these costs must be developed. If lanthanum precipitate can be collected, and then lanthanum regenerated so that it could be recycled for further phosphate precipitation, then the operating expenses for this type of phosphorus removal process would be independent of lanthanum costs, no matter how high these may be, aside from the initial purchase of lanthanum, and any lanthanum make-up costs.

It is the objective of this research to examine a lanthanum regeneration process - the various reactions and separation techniques required, the kinetics and yields of the reactions, and the overall technical feasibility of regeneration following precipitation of phosphates by lanthanum.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2-1. Introduction

Various researchers(1,2) feel that eutrophication, a process which involves an increase in the biologic productivity of a body of water as a result of nutrient enrichment from natural sources or man-made pollution, can be checked by the control of such key nutrients as carbon, nitrogen, and phosphorus.

Of the key nutrients, carbon (as CO_2) is always present in the atmosphere, while nitrogen can be fixed by blue-green algae. Thus, some researchers(3) emphasize the importance of removal of phosphates from waste-waters and detergents in order to control eutrophication. Furthermore, there is some evidence(4,5) that removal of phosphate sources will improve the condition of lakes.

Although phosphates enter the waterways(6) from natural sources, in run-off from cultivated and urban areas, and from domestic sewage, government programs are committed to phosphate removal at the sewage treatment plant.

A number of nutrient removal treatment methods have been investigated(7-10). The ones most frequently mentioned in state-of-the-art reviews(11,12) are based on chemical precipitation of phosphates. This is commonly accomplished at present by addition of lime, alum, or iron either to treatment plant effluent, or directly in conjunction with the conventional sedimentation and biological treatment process schemes. Basic drawbacks of these processes as they are operated at present time are the high usage of chemicals, disposal of the higher sludge volume created, and problems with biological-chemical sludge in digesters.

Recht and Ghassemi(13) used lanthanum salts to precipitate orthophosphates and polyphosphates from water. Their work indicated that lanthanum (111) shows a broader effective pH range and lower residual phosphate concentration than Al (111). Since current lanthanum costs are much higher than those of aluminum, the only way for it to become attractive for phosphate precipitation is either with reduced costs due to an increased market, or if La could be recovered and reused.

Spent precipitant recovery has been studied(14,15,16) for lime and aluminum phosphate precipitation, but found successful only for the former.

2-2. What is Lanthanum?

Lanthanum (La) is a member of the lanthanides, or rare earth elements, which are the largest naturally occurring group in the periodic table. It has the atomic number 57 and an atomic weight of 138.91.

Lanthanum, a so-called rare earth, is not rare. Table I from Goldschmidt(17) which compares the abundance of lanthanum with other elements in igneous rocks shows that lanthanum is more abundant than lead,

TABLE 1*

Comparison of Abundance of Lanthanum and Other Elements in Igneous Rocks

Element	Atomic Number	Abundance g/ton
La	57	19
Co	27	40
Ni	28	100
Zn	30	40
Pb	82	16
Ag	47	0.1
Au	79	0.005

* After Goldschmidt(17)

and certainly many times as abundant as silver or gold. The rare earths are widely scattered in nature in low concentrations, and they occur in a number of concentrated minerals such as monazite, xenotime, bastnasite and gadolinite(18).

Separation of rare earths at present is accomplished primarily by three methods: fractional crystallization, liquid-liquid extraction, and ion exchange.

Present uses of rare earths are in magnesium, chromium, and ferrous alloys, in polishing and coloring of glass, and in manufacture of carbon-arc electrodes.

2-3. Lanthanum as a Precipitant of Phosphate

Work by Recht, Ghassemi, and Kleber(19) revealed a new possible use of rare earth ions as the precipitating cation to remove simple and condensed phosphates from waste-waters.

Recht et al.(13) conducted a parametric study of phosphate precipitation, and compared the results with data obtained using aluminum salts. A summary of their findings follows.

2-3-1. Lanthanum Precipitation of Orthophosphates in Distilled Water

Figure 1 shows that, at a 0.5:1 La to PO_4 molar ratio, the residual phosphate concentration was around 5 mg/l P in the pH range from 4 to 9.

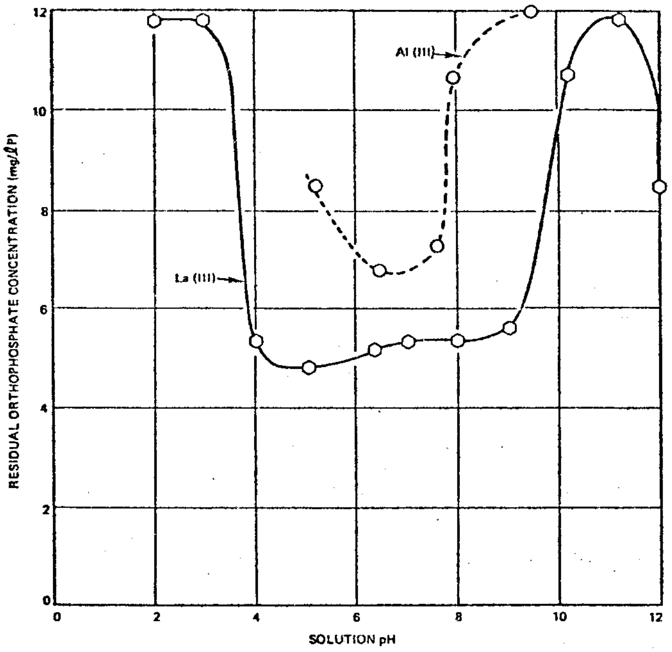

Figure 1. Orthophosphate Precipitation at 0.5:1 Cation-to-Phosphate Molar Ratio; Initial Concentration, 12 mg/ℓ P Na_2HPO_4

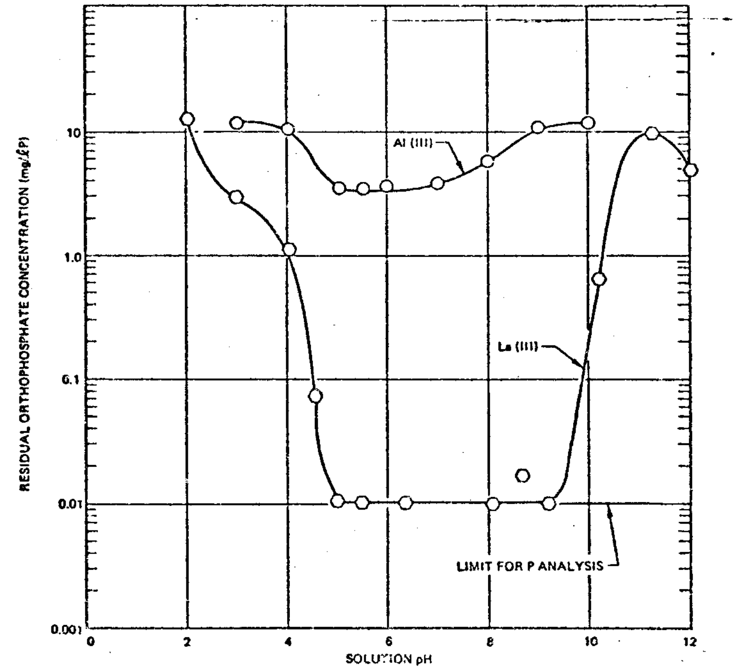

Figure 2. Orthophosphate Precipitation at 1:1 Cation-to-Phosphate Molar Ratio; Initial Concentration, 12 mg/ℓ P Na_2HPO_4

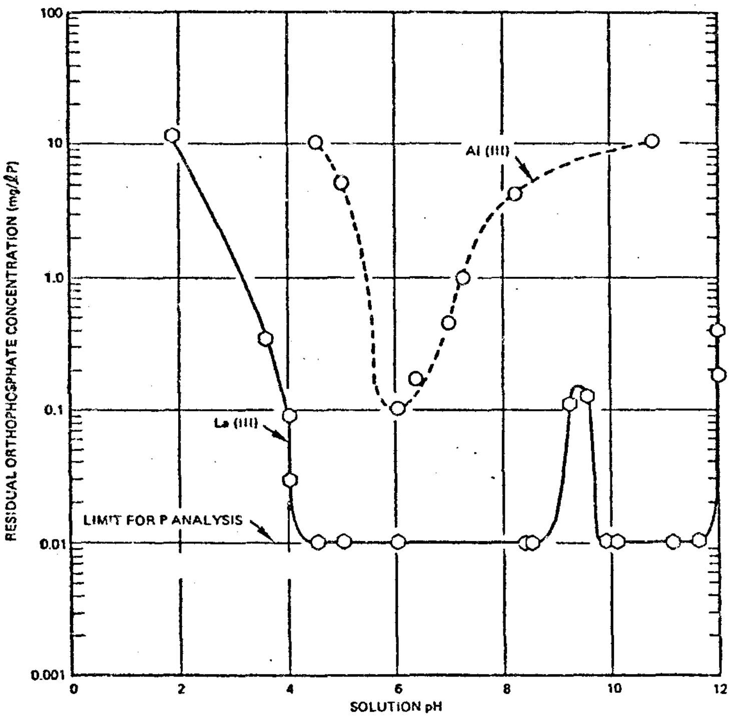

Figure 3. Orthophosphate Precipitation at 2:1 Cation-to-Phosphate Molar Ratio; Initial Concentration, 12 mg/ℓ P Na_2HPO_4

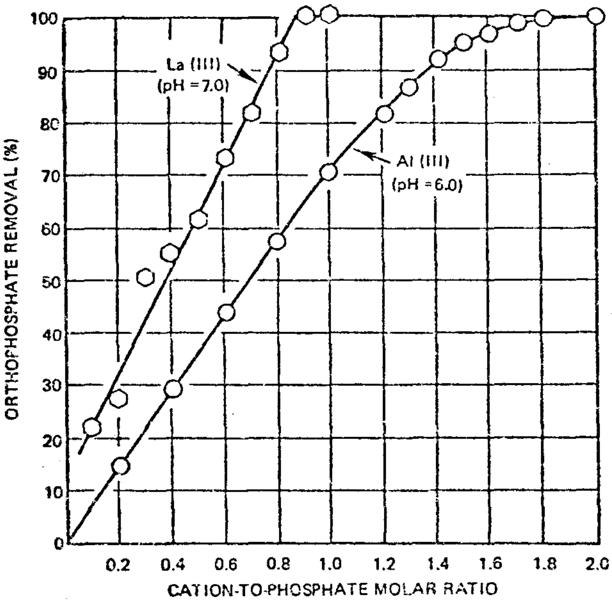

Figure 4. Orthophosphate Precipitation at Constant pH; Initial Concentration, 12 mg/ℓ P Na_2HPO_4

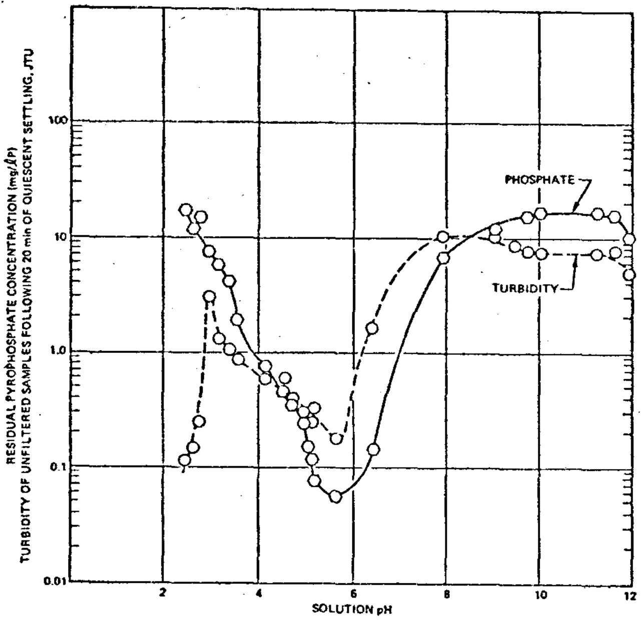

Figure 5. Pyrophosphate Precipitation at 1:1 Lanthanum-to-Phosphate Equivalence Ratio; Initial Concentration, 18 mg/ℓ P $Na_4P_2O_7$

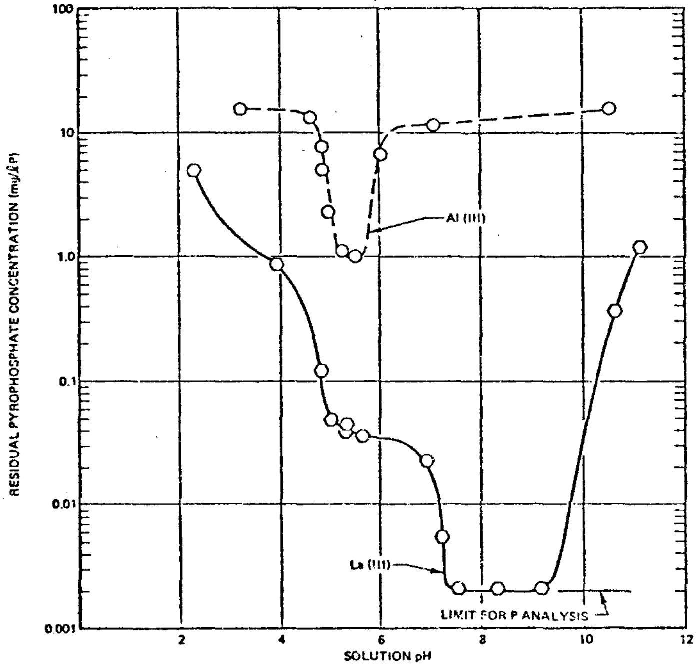

Figure 6. Pyrophosphate Precipitation at 2:1 Cation-to-Phosphate Equivalence Ratio; Initial Concentration, 18 mg/ℓ P $Na_4P_2O_7$

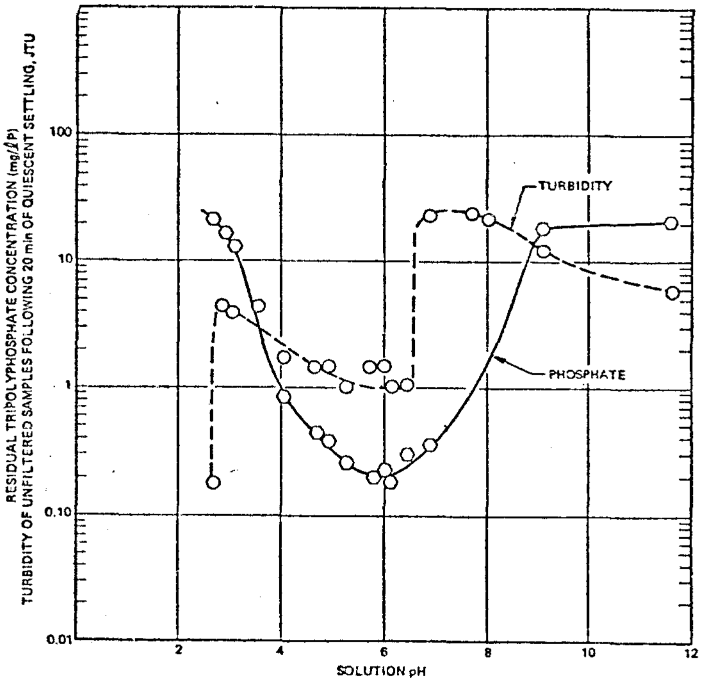

Figure 7. Tripolyphosphate Precipitation at 1:1 Lanthanum-to-Phosphate Equivalence Ratio; Initial Concentration, 21.6 mg/ℓ P $Na_5P_3O_{10}$

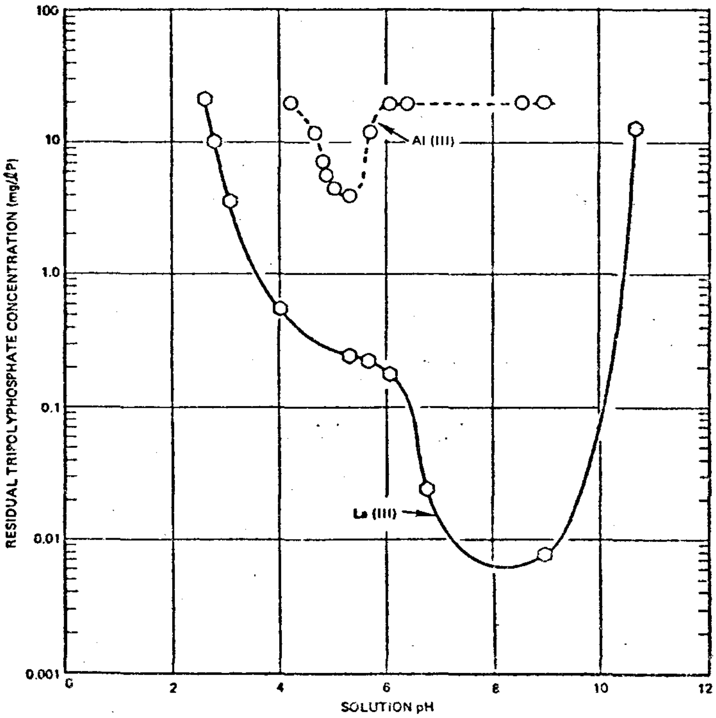

Figure 8. Tripolyphosphate Precipitation at 2:1 Cation-to-Phosphate Equivalence Ratio; Initial Concentration, 21.6 mg/ℓ P $Na_5P_3O_{10}$

At a 1:1 La to PO_4 ratio, the phosphate removal was greatest in the pH range 5 to 9. Almost complete removal of phosphate was achieved (Figure 2).

At a 2:1 La to PO_4 ratio, two pH regions of good phosphate removal occur -- one from pH 4 to pH 9, and another in pH range 9.7 to 11.5. Again, almost complete removal of phosphate is achieved in these regions (Figure 3).

When phosphate precipitation with lanthanum was carried out at a constant pH of 7.0 (Figure 4), complete removal of phosphate was achieved at La:PO_4 molar ratios as low as 0.9. In the 0.1 - 0.9 molar ratio range, the removal of phosphate was directly proportional to the amount of added lanthanum.

2-3-2. Lanthanum Precipitation of Condensed Phosphates

As with precipitation of orthophosphates, the extent of condensed phosphate removal with lanthanum is dependent on solution pH and reactant ratios. The optimum precipitation pH range for both pyrophosphate and for tripolyphosphate lies in the range 5.0 to 6.5 at a 1:1 La-PO_4 molar ratio, and 7 to 9 at a 2:1 ratio (Figures 5 - 8).

2-3-3. Lanthanum Precipitation of Phosphates from Secondary Effluent

Phosphate removal from waste-water exhibits a dependence on pH similar to the phosphate removal from pure solutions. With the secondary

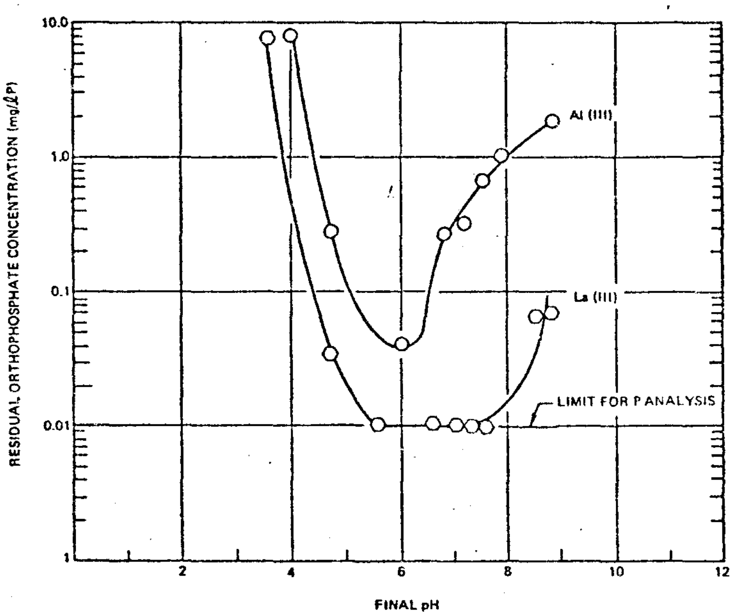

Figure 9. Phosphate Precipitation from Secondary Effluent at 2:1 Cation-to-Phosphate Molar Ratio; Initial Concentration, 7.75 mg/ℓ P; Initial pH = 7.8

Figures 1 to 9 after Recht et al(19)

effluent, a minimum residual phosphate concentration of 0.01 mg/l P or less was obtained in the 5.6 to 7.6 pH range (Figure 9). Also, the residual phosphate concentration was less than 0.1 mg/l P in the 4.4 to 8.8 pH range. As with pure phosphate solutions, the optimum pH for phosphate removal from waste-water with lanthanum is fairly broad and includes those pH levels normally encountered in the effluents from biological waste-water treatment plants.

Despite the use of excess lanthanum (a 2:1 La/PO_4 molar ratio), no lanthanum was detected in the filtrate. The fact that the excess lanthanum is precipitated is of importance, since in practice an excess of lanthanum could be used to ensure complete removal of phosphate without any significant loss of the lanthanum in the effluent waste-water.

2-3-4 Effectiveness of Lanthanum and Aluminum

Recht et al.(13) compared the lanthanum precipitation results with similar data obtained using aluminum salts. Lanthanum gives superior performance in the following ways.

The pH range for optimum removal of phosphate with lanthanum is considerably broader than that for aluminum.

Lanthanum is more effective than aluminum for precipitation of phosphates. At a pH of 7.0 (Figure 4), essentially complete removal of orthophosphate was obtained with a lanthanum to orthophosphate molar ratio of 0.9:1.0. With aluminum, on the other hand, minimum residual phosphate concentrations observed at 1:1 and 2:1 Al/PO_4 molar ratios were

3.5 mg/l P and 0.1 mg/l P, respectively.

As indicated in Figures 6 and 8, lanthanum is similarly more effective than aluminum in the precipitation of pyrophosphate, and tripolyphosphate.

For precipitation of phosphates from secondary effluent, the pH range for optimum phosphate precipitation with aluminum lies below pH 7. The effectiveness of lanthanum for phosphate removal extends well above pH 7, and includes those pH levels normally encountered in domestic waste-water.

In all cases, the lanthanum precipitation reactions were complete within a few seconds.

2-4. Regeneration of Lanthanum from Precipitate

Recht et al.(20) have suggested the following sequence of steps for the phosphate removal process:

1. Phosphate Precipitation: Lanthanum is added to the waste-water as $LaCl_3$ or $La_2(SO_4)_3$. The La (111) ions react with the soluble phosphate forming an insoluble precipitate:

$$La^{+3} + PO_4^{-3} \rightarrow LaPO_4 \downarrow$$

2. Precipitate Removal: The insoluble $LaPO_4$ is removed from the water and collected by sand or charcoal filtration, or other equivalent operation. This completes the water treatment part of the

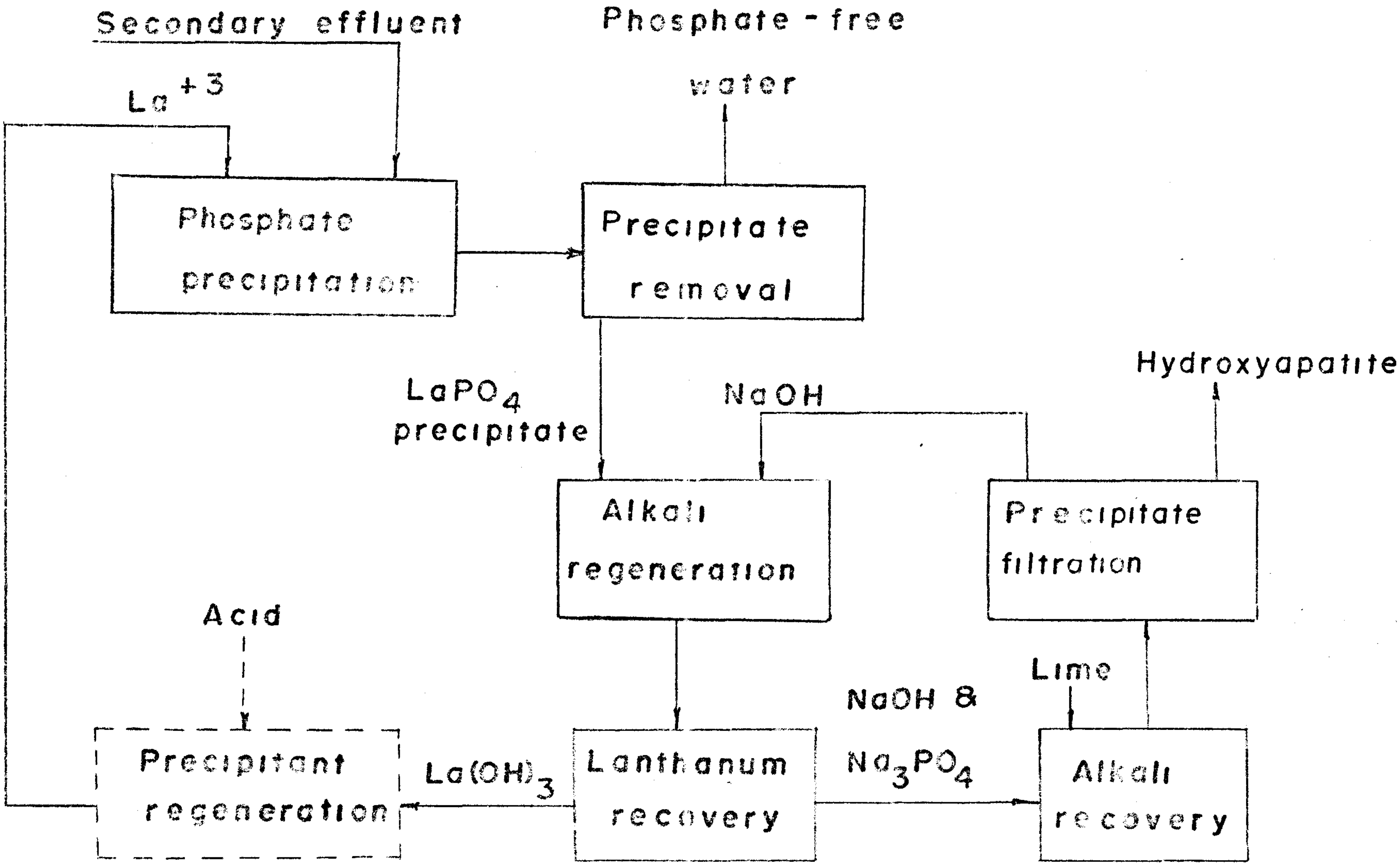

Figure 10 - Phosphate removal process as suggested by Recht et al[19].

process; the purified water stream leaves the treatment plant after the precipitate removal step.

3. Alkali Regeneration: The insoluble $LaPO_4$ is treated with aqueous NaOH to convert the $LaPO_4$ to insoluble $La(OH)_3$ and produce soluble Na_3PO_4.

$$LaPO_4 + 3\ NaOH\ (aq) \rightarrow La(OH)_3 \downarrow + Na_3PO_4\ (aq)$$

4. Lanthanum Recovery: The insoluble $La(OH)_3$ is separated from the solution of NaOH and Na_3PO_4 by charcoal filtration, or an equivalent operation.

5. Precipitant Regeneration: The $La(OH)_3$ may be used directly in acidic water of significant buffer capacity or if necessary be reacted with HCl or H_2SO_4 to form soluble $LaCl_3$ or $La_2(SO_4)_3$ for return to the process at Step 2.

6. Alkali Recovery: The NaOH solution containing Na_3PO_4 from Step 4 is treated with lime to form an insoluble precipitate of $Ca_{10}(OH)_2(PO_4)_6$. This precipitate is then removed by filtration (or an equivalent operation) so the reconstituted NaOH solution can be returned to Step 3.

$$6\ Na_3PO_4\ (aq) + 10\ Ca(OH)_2 \rightarrow Ca_{10}\ (OH)_2\ (PO_4)_6 + 18\ NaOH$$

2-5. Research Objective:

Recht et al[20] have described their experiments in precipitation of phosphates with lanthanum, and have suggested a regeneration process. It is the objective of this research project to

a) Carry out the suggested regeneration reactions on a batch-type bench scale study and determine which reactions can take place, and under which conditions of stoichiometry and temperature.

b) Determine the feasibility of the regeneration reactions from the point of view of yields and kinetics of reactions.

c) Examine some techniques for phase separation of reacted reagents.

d) Perform material balances on the process to get an indication of the cost of chemicals and sizes of reactors required as well as amount of sludge produced, and amounts of make-up chemicals required.

CHAPTER III

EXPERIMENTAL APPROACH AND PROCEDURE

Regeneration of lanthanum was considered as a series of five separate operations:

a) Precipitation of $LaPO_4$ from distilled and waste-waters.

b) Separation of La from PO_4 by alkali.

c) Resolubilization of La for return to Process.

d) Precipitation of PO_4 from alkali with lime.

e) Regeneration and make-up of alkali.

Each operation was examined, and batch-type bench scale experiments were used to obtain reaction data for the chemical reactions involved.

The first step in the regeneration studies was to determine whether the reactions proposed, i.e., alkali separation of PO_4 from $LaPO_4$, and lime precipitation of PO_4 from alkali are feasible, and if so, under what conditions.

Orthophosphate added to distilled water was reacted with lanthanum, and the precipitated lanthanum phosphate was settled and concentrated by centrifuging. The resulting $LaPO_4$ slurry was then reacted with alkali of different molar strengths (2M to 14M). The results showed that for equal reaction times, the higher strength alkali led to higher reaction completion. Furthermore, when different volumetric ratios of alkali to slurry were used, it appeared that the higher alkali to slurry ratios led to higher reaction completion.

Based on results of these experiments, lime was added to 6M NaOH with 2250 ppm PO_4 in solution. No precipitation of phosphates occurred even when an excess of lime was used. Other means were tried to obtain precipitation of phosphates:

a) KOH was used in place of NaOH.

b) Reagents such as alum and ferric chloride were used in place of lime.

c) The temperature of 6M NaOH was lowered to crystallize a sodium phosphate compound.

d) Lime was added to precipitate phosphates from lower strength (3M) NaOH.

The two latter efforts produced satisfactory results, and additional experiments were conducted to determine how the lower strength NaOH affects the NaOH-$LaPO_4$ reaction, and the effect of different slurry to NaOH volumetric ratios.

It was found that 3M NaOH was satisfactory as far as the yield of the reaction was concerned; however the reaction was quite slow -- about 5 - 6 hours. Therefore, the temperature of the alkali used was raised, and this produced a reduction in reaction time to less than 1/2 hour for both the NaOH-$LaPO_4$ reaction and the lime-phosphate precipitation.

Addition of stoichiometric ratio of lime to PO_4 for phosphate precipitation from alkali left a phosphate residual in the alkali, which, it was found, is detrimental to the $LaPO_4$-NaOH reaction when the alkali is recycled. Use of excess lime, however, resulted in practically complete phosphate precipitation.

The $La(OH)_3$ precipitate which forms as a result of the $LaPO_4$-NaOH reaction was treated with acid to resolubilize lanthanum for return to the process. It was found that either HCl or H_2SO_4 could be used, and that the reaction is quite rapid.

In the second phase of the study, phosphates were precipitated from secondary effluent with lanthanum, and regeneration studies conducted on the lanthanum phosphate precipitate. The results obtained were similar to those obtained with lanthanum phosphate precipitated from distilled water.

Finally, process design calculations were performed to show the engineering feasibility of the lanthanum regeneration process.

CHAPTER IV

PHASE I - DISTILLED WATER EXPERIMENTS

4-1. Preliminary Experiments

4-1-1. Phosphate Precipitation

Phosphate precipitation was performed batch-wise with equipment shown in Figure 11.

The procedure followed was: 20 l of distilled water were poured into the settling tank. To this, 4.3 ml of 2.99M H_3PO_4 acid was added (orthophosphoric acid was used as phosphate source because of ease of measuring and mixing), bringing the concentration of the solution to 20 mg/l P. The pH was adjusted to 7 using NaOH and HCl.

Lanthanum was added in the form $La(NO_3)_3.5H_2O$ in a 1:1 La/PO_4 molar ratio (5.34 gms as $La(NO_3)_3.5H_2O$). The water was rapidly mixed (paddle rate = 150 rpm) for 5 minutes. As the lanthanum crystals dissolved, the pH was continuously adjusted to 7. Following rapid mix, the mixing rate was slowed down to 50 rpm, and mixing continued at this rate for 20 minutes. The mixing was then stopped, and the $LaPO_4$ precipitate formed allowed to settle for about 45 minutes. During this time, the $LaPO_4$ settled slowly forming white, fluffy floc about 1/8 of an inch in diameter. At the end of the settling period, the cleared water was drained, and the precipitated $LaPO_4$ transferred from the settling tank to a flask.

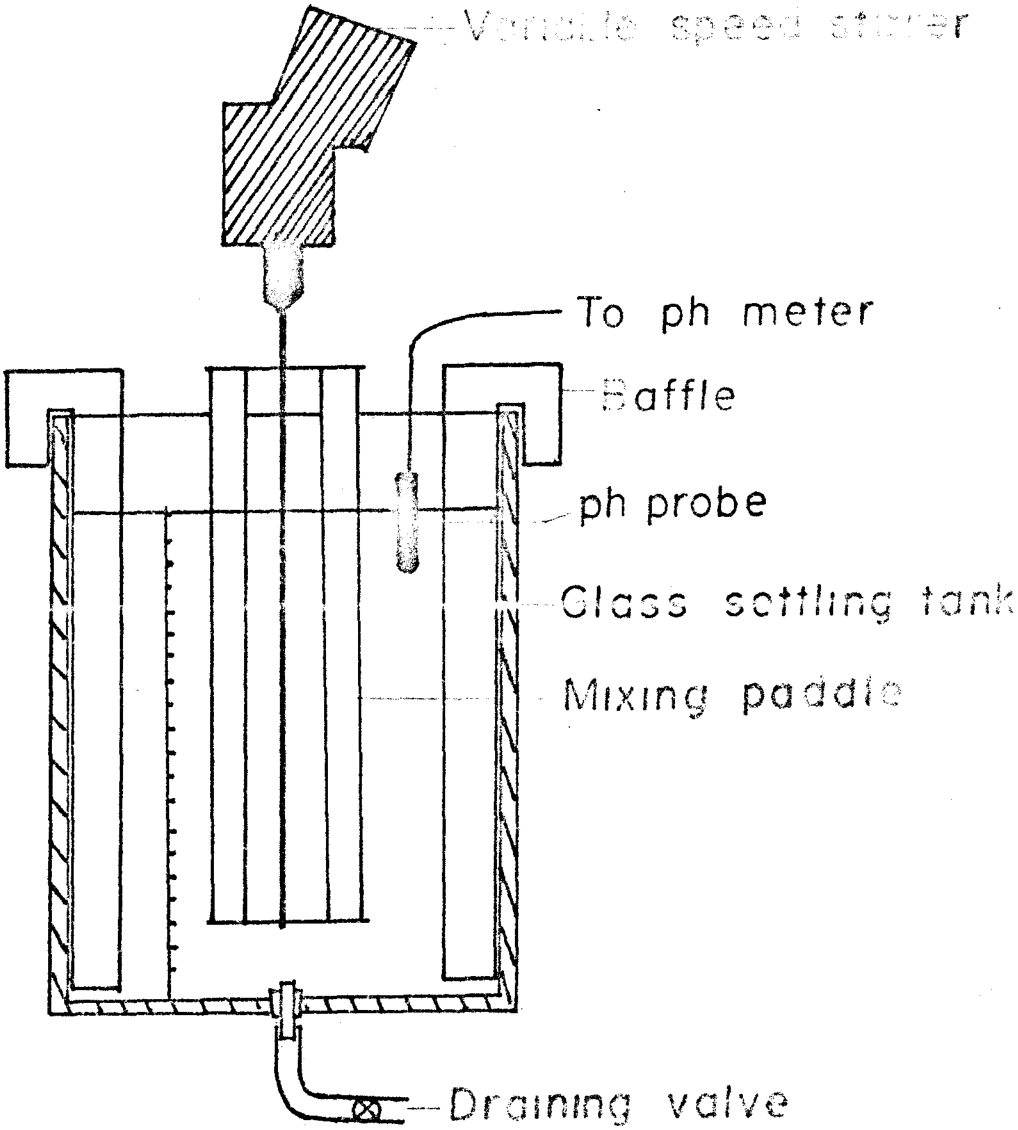

Figure 11 - Phosphate precipitation equipment

The floc formed was very fragile, and broke into very fine particles during transfer from the settling tank. However, it reformed in the flask.

Solids determination (Appendix I) performed on the settled floc showed a solids content of about 2000 ppm $LaPO_4$.

4-1-2. $LaPO_4$ Concentration

Although settling brought about some separation of $LaPO_4$ from water, the settled floc still contained more than 99% water. Because the next stage in the regeneration procedure involves reacting concentrated alkali with the $LaPO_4$ floc, it is obvious that considerable dilution of alkali would occur.

To reduce the dilution, further separation of the $LaPO_4$ precipitate from water is necessary. Because the floc is very fragile, and easily broken, such separation techniques as filtering would not be successful unless a very fine pore size was used. Therefore, the slurry was concentrated by centrifuging.

4-1-3. Centrifuge Tests

A Lourdes Model LRA centrifuge with VRA #1200 rotor was used for concentrating of $LaPO_4$ floc. Tests were run varying the rotor speed, and centrifuging time. Table 2 shows results of these tests.

TABLE 2

Solids Concentration at Various RPM and Centrifuging Times

RPM	RCF x G	Time (min)	Solids Concentration
3000	1460	10	32,000 ppm
3000	1460	30	42,000 ppm
6000	5900	10	41,700 ppm
6000	5900	30	68,000 ppm

Based on these tests, operating conditions chosen for future separation work were: 6000 RPM rotor speed, 30 minutes centrifuging time.

The $LaPO_4$ at a concentration of 68,000 ppm had a slurry-like consistancy, and flowed easily.

4-2. Alkali Reaction with Lanthanum

Procedure:

Before each run, the density and solids concentration of the $LaPO_4$ slurry was determined. An amount of slurry was then weighed out into an Erlenmayer flask, and NaOH of known molarity added to the flask. The magnetically stirred reagents were allowed to react together for a certain period of time, at the end of which a sample of the products was withdrawn, and centrifuged in an International Clinical model centrifuge at a medium setting for 5 minutes. This produced two phases -- a liquid phase made up of aqueous NaOH with PO_4^{-3}, and a solid phase -- mostly $La(OH)_3$. A sample of the liquid phase was then withdrawn for phosphate analysis.

Results:

In preliminary studies, reactions were run for 20 minute time intervals, at room temperature (about 25°C) varying the molarity of NaOH, and $NaOH/LaPO_4$ slurry volumetric ratio.

A series of runs using a slurry of 5900 ppm $LaPO_4$ concentration, at a NaOH/slurry volumetric ratio 1:1 gave the results shown in Figure 12 and Table 3. From these, it can be concluded that the strength of NaOH used has a significant effect on the NaOH-lanthanum phosphate reaction.

Another series of runs using $LaPO_4$ slurry at 67,000 ppm $LaPO_4$, and constant initial NaOH molarity (6M) gave the results shown in Figure 13 and Table 4. These show that the NaOH/$LaPO_4$ slurry ratio used affects the yield of the reaction.

Thus, the NaOH-$LaPO_4$ reaction goes quite close to completion when the suitable alkali strength, and NaOH/$LaPO_4$ slurry ratio are selected.

(Effective molarity is the strength of NaOH after dilution with the $LaPO_4$ slurry water, (PO_4) for total removal is calculated from the slurry concentration coming in -- thus, if a slurry of 67,000 ppm $LaPO_4$ concentration is used with 6M NaOH at NaOH/slurry ratio of 2:1, then the (PO_4), i.e., phosphate concentration, for total removal is:

$$\text{67,000 ppm} \quad \times \quad \frac{1}{2.46} \quad \times \quad \frac{1}{3} \quad = \text{9100 ppm}$$

$$(LaPO_4) \quad \times \quad \frac{(PO_4)}{(LaPO_4)} \quad \times \quad \frac{\text{Volume of slurry}}{\text{Volume of alkali + slurry}}$$

and effective molarity is:

$$6M \times \frac{2}{3} \quad \frac{\text{Volume of NaOH}}{\text{Volume of NaOH + slurry}} = 4M)$$

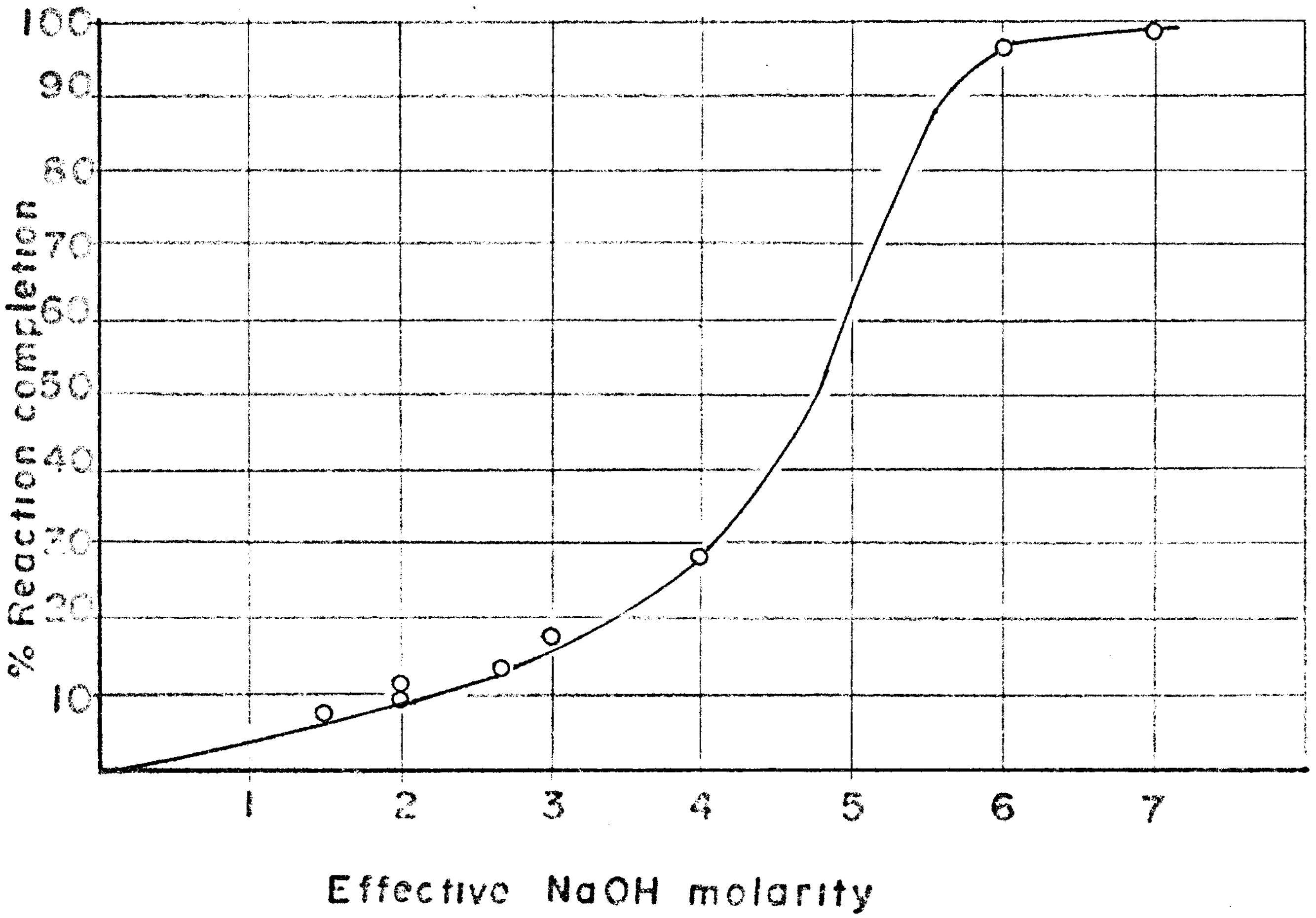

Figure 12 - Effect of NaOH molarity on NaOH-$LaPO_4$ reaction

TABLE 3

Effect of NaOH Molarity on NaOH-$LaPO_4$ Reaction

Reaction Time - 20 minutes

Initial Phosphates = 2410 ppm PO_4

NaOH	$LaPO_4$ Slurry	Final (PO_4) in Alkali	Effective Molarity	% PO_4^{-3} Removal
20 ml 14M	20 ml	2370	7M	98.5%
20 ml 12M	20 ml	2320	6M	96.2%
50 ml 8M	50 ml	695	4M	28.8%
50 ml 6M	50 ml	430	3M	17.85%
100 ml 4M	50 ml	330	2.67M	13.65%
50 ml 4M	50 ml	240	2M	9.95%
100 ml 3M	50 ml	270	2M	11.2%
50 ml 3M	50 ml	170	1.5M	7.05%

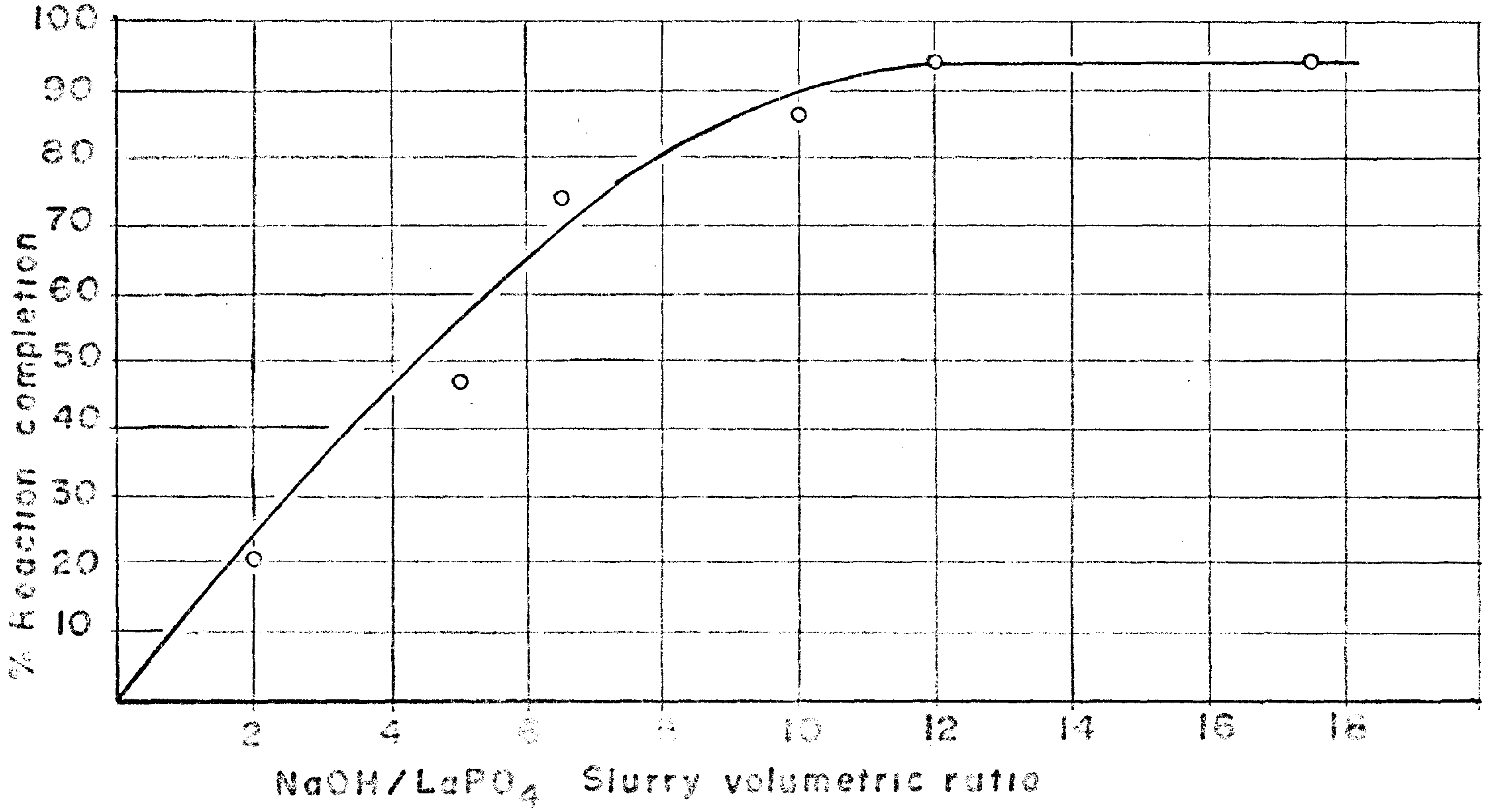

Figure 13 - Effect of NaOH/LaPO$_4$ SLURRY Volumetric ratio on NaOH-LaPO$_4$ reaction

TABLE 4

Effect of NaOH-$LaPO_4$ Slurry Ratio

Reaction Time - 20 minutes

Reagents: 6M NaOH, 67,000 ppm $LaPO_4$ slurry

NaOH/Slurry Ratio	Effective Molarity	(PO_4) for 100% Completion	Actual (PO_4) ppm	% PO_4 Removal
2.0	4 M	9100	1900	20.9
5.0	5 M	4560	2150	47.0
6.5	5.2M	3770	2800	74.25
10.0	5.45M	2490	2150	86.3
12.0	5.54 M	2175	2050	94.4
17.5	5.67 M	1532	1450	94.6

An unexpected phenomenon observed at low NaOH/slurry ratios (6.5:1 and less) when the molarity of the NaOH used was 6M or higher was the formation of fine, spiky crystals. Findings in literature (Figure 14) indicate this to be caused by the low solubility of PO_4 in high strength NaOH, resulting in crystallizing out of sodium phosphate compounds.

4-3. Phosphate Removal from Alkali by Lime

Procedure:

To known volume of NaOH, orthophosphoric acid was added to get a predetermined PO_4 concentration in the alkali. Since the phosphate removal reaction is assumed to be:

$$6\ Na_3PO_4\ (aq) + 10\ Ca(OH)_2 \rightarrow Ca_{10}(OH)_2(PO_4)_6\downarrow + 18\ NaOH$$

$Ca(OH)_2$ was added in amounts such that Ca:PO_4 molar ratio was 10:6.

The magnetically stirred reagents were allowed to react together, and periodically a sample was withdrawn and centrifuged in an International Clinical model centrifuge at a medium setting for 5 minutes. This produced two phases -- a liquid phase made up of aqueous NaOH, and a solid phase containing such calcium phosphate compounds as were produced. A sample of the liquid phase was then analyzed for phosphates.

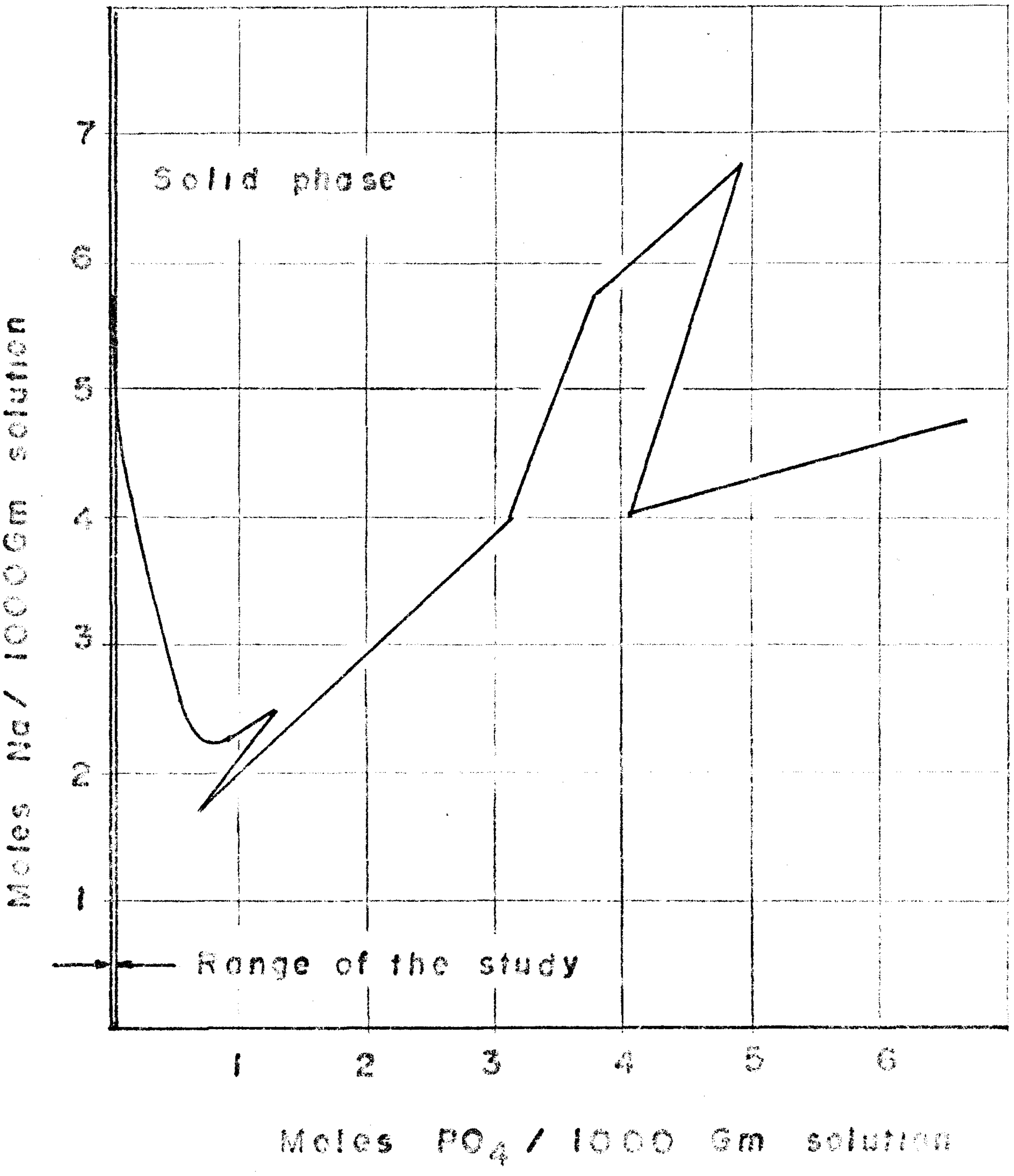

Figure 14 - Solubility of PO_4 in NaOH-after Seidell[21]
System: NaOH, H_3PO_4, H_2O @ 29°C

Results:

From the preceding experiments (Section 4-2), it appeared that NaOH of high molarity should be used to obtain adequate conversion levels of $LaPO_4$ to $La(OH)_3$. Therefore, the alkali recovery experiments were carried out with 6M NaOH, at $Ca:PO_4 = 10:6$ and 20:6 (excess of calcium). Results are summarized in Table 5. Thus, in three hours of reaction, there was no precipitation of phosphate.

4-4. Alternative Reactions

4-4-1. Increase of Phosphate Level in Alkali

One possible explanation for the lack of phosphate precipitation from alkali in the previous reaction is that the phosphate level is too low to initiate the reaction at such high NaOH concentrations.

However, as found earlier (Section 4-2, Figure 14), the solubility of phosphate in high strength NaOH is quite low, and any excess phosphate comes out of solution as a sodium phosphate compound. Thus, phosphate concentrations higher than about 2200 ppm are impossible to achieve with NaOH of high molarity.

The $KOH-PO_4$ system (Figure 15) has no solubility limit for PO_4 in the range considered here for KOH solutions up to 9.5 molar. The alkali-lanthanum and lime-alkali reactions were repeated, therefore, using KOH and same procedures as above. Tables 6 and 7 summarize the results.

TABLE 5

Alkali Recovery Experiments - Results

Time (minutes)	Phosphate Concentration in Alkali (ppm)	
	$Ca:PO_4$ = 10:6	$Ca:PO_4$ = 20:6
0	2250	2250
10	2250	2250
20	2250	2250
30	2250	2250
60	2250	2250
90	2250	2250
120	2250	2250
180	2250	2250

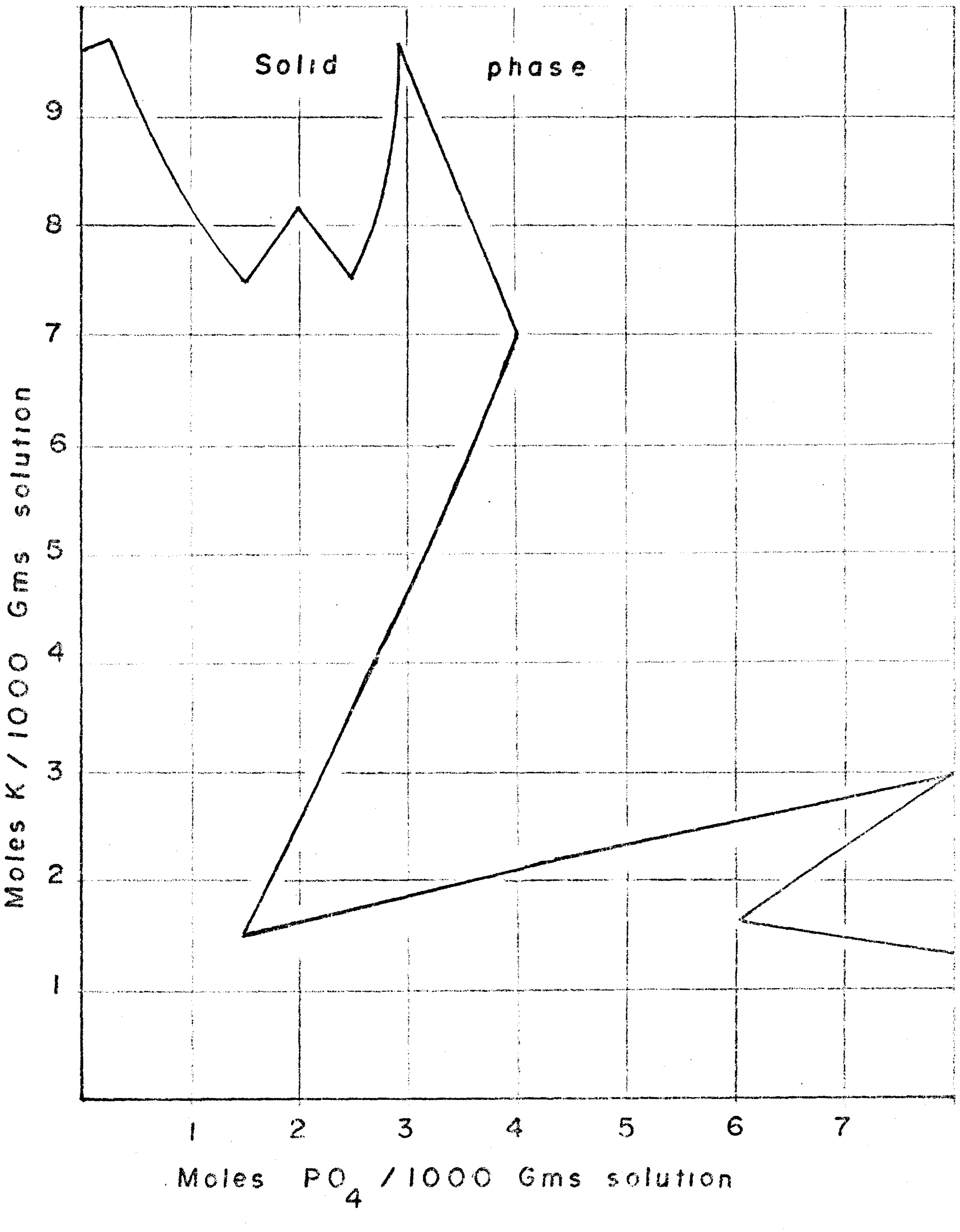

Figure 15 - Solubility of PO_4 in KOH-after Seidell[21]
System: KOH, H_3PO_4, H_2O

TABLE 6

Alkali-$LaPO_4$ Reactions

Initial KOH = 6M

KOH/slurry Ratio	Effective Molarity	(PO_4^{-3}) for Total Removal	Actual (PO_4^{-3})	% Completion
1	3M	14,350	1175	8.1
2	4M	9,560	1200	12.5
5	5M	4,780	1600	33.5
10	5.46M	2,610	1400	53.7

TABLE 7

Alkali-$LaPO_4$ Reactions

Initial KOH = 8M

KOH/slurry Ratio	Effective Molarity	(PO_4^{-3}) for Total Removal	Actual (PO_4^{-3})	% Completion
1	4M	14,350	1125	7.9
2	5.34M	9,560	1675	17.5
5	6.67M	4,780	1825	38.3
10	7.28M	2,610	1400	53.7

A comparison of these results with those in Table 4 indicates that the KOH-$LaPO_4$ reaction is much less complete than the NaOH-$LaPO_4$ reaction. Furthermore, from Table 8, it is apparent that there is no better precipitation of phosphates from alkali when KOH is used in place of NaOH. Therefore, KOH was rejected as a substitute for NaOH.

4-4-2. Use of Other Reagents in Place of Lime

Since there was no removal of phosphates with lime in the alkali recovery reaction, other reagents commonly used for precipitation of phosphates from waste-waters were considered. Results of this series of experiments are summarized in Table 8. A PO_4 /reagent molar ratio of 1:1 was used. Although about 40% removal of PO_4 occurred at the end of 48 hours when the NaOH was used, these reactions were considered to be too slow to be of use and further alternatives were looked at.

4-4-3. Crystallization of Phosphates

Generally, the solubility of solids in liquids decreases with temperature. Therefore, by lowering the temperature of alkali following the separation of $La(OH)_3$ precipitate from NaOH, removal of phosphate could be obtained by crystallization. To determine the extent of PO_4 removal by this method, the following experiment was carried out.

To two flasks, one containing 6M NaOH, the other 8M NaOH, orthophosphoric acid was added to bring the concentration of the solution to 2000 ppm PO_4.

TABLE 8

Alkali Recovery Reaction: Results of Using Various Reagents

Alkali Used	Reagent	(PO_4) Residual in Alkali (ppm) Time 0	1 hr.	2 hr.	48 hr.
6M KOH	$CaCl_2$	2030	2030	2030	1600
6M KOH	$Ca(OH)_2$	2030	2030	2030	2030
6M KOH	$Al(OH)_3$	2030	2030	2030	2030
6M KOH	$FeCl_3$	2030	2030	2030	2030
6M NaOH	$CaCl_2$	1980	1790	1750	1160
6M NaOH	$Al(OH)_3$	1980	1790	1750	1160
6M NaOH	$FeCl_3$	1980	1815	1790	1160

The flasks were then refrigerated at a temperature of -17°C. The results (Table 9) show that over 90% phosphate removal occurred. Thus, crystallization looks like a feasible method of phosphate removal from alkali.

4-4-4. Use of Lower Strength Alkali

Phosphate precipitation from waste-waters with lime is quite effective at high pH levels -- $\sim$ pH 10 (see Section 2-1). However, it is very probable that high NaOH concentrations (6M or more) are detrimental to this reaction. To evaluate the effect of lower NaOH concentration on phosphate removal from alkali, kinetic tests were run using 3M NaOH, and different starting phosphate concentrations.

From the results in Figure 16, it appears that significant phosphate removal (70 - 80%) takes place at these conditions. Furthermore, the residual phosphate concentration is a function of the initial phosphate concentration.

When an excess of lime is used (Figure 17), almost complete phosphate removal results.

4-5. Effect of Lower Strength Alkali on NaOH-$LaPO_4$ Reaction

To determine the effect of lower strength NaOH on the NaOH-$LaPO_4$ reaction, kinetic tests were run using 2, 3, and 4M NaOH, at NaOH/slurry ratios as indicated.

TABLE 9

Decrease of PO_4 Concentration from Alkali as a Result of Crystallization

	(PO_4) - ppm	
	6M NaOH	8M NaOH
Initial	2000	2000
After Crystallization	160	175

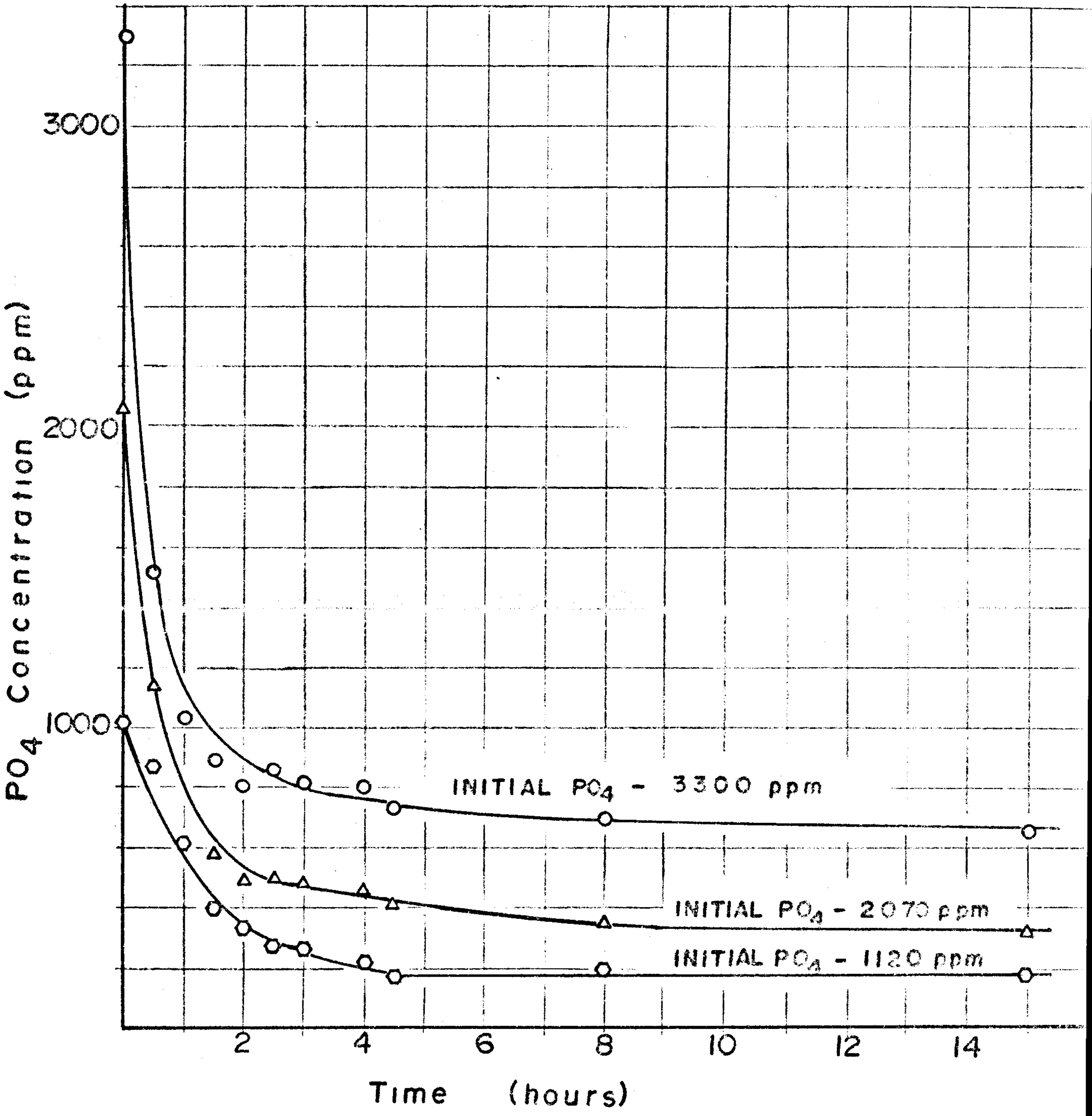

Figure 16 - Removal of PO_4 with $Ca(OH)_2$ from 3M NaOH
$Ca:PO_4$ molar ratio = 10:6 @ 20°C

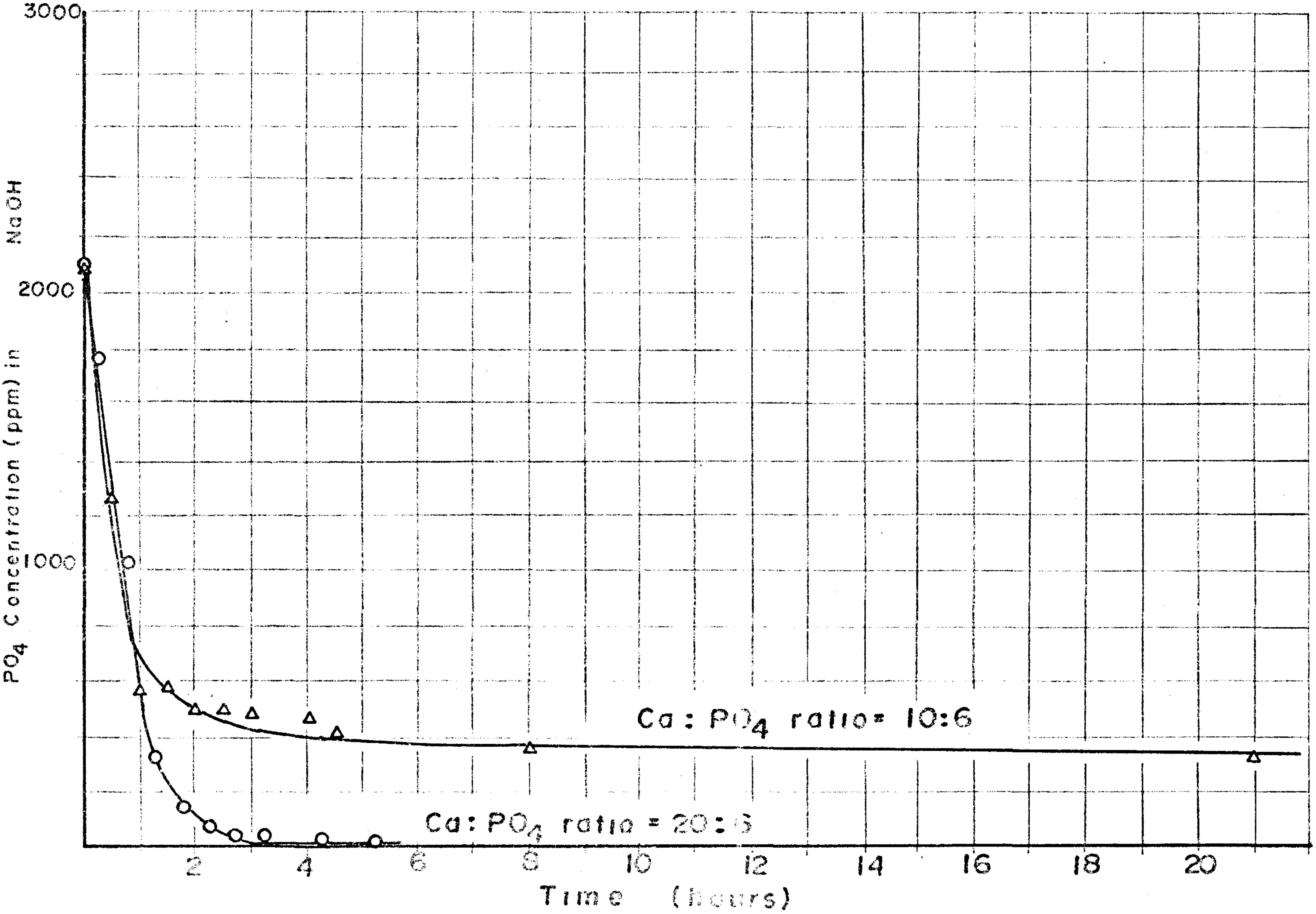

Figure 17 - Effect of excess $Ca(OH)_2$ on removal of phosphate from NaOH

TABLE 10

Kinetic Studies on PO_4 Removal with $Ca(OH)_2$ From 3M NaOH, T = 20°C

10-A: $Ca:PO_4$ = 10:6 (molar ratio)

Time	(PO_4) Residual in Alkali (ppm)			
0	3300	2070	1120	500
0.5 hrs.	1520	1250	870	500
1.0	1030	570	620	410
1.5	900	580	400	480
2.0	810	500	340	400
2.5	860	500	280	420
3.0	820	485	270	440
4.0	800	460	235	310
4.5	730	405	175	300
8.0	700	355	200	200
21.0	650	320	175	120

10-B: $Ca:PO_4$ = 20:6 (molar ratio)

Time	(PO_4) Residual in Alkali (ppm)
0	2100
0.25 hrs.	1770
0.75	1020
1.25	305
1.75	145
2.25	75
2.75	55
3.25	40
4.25	31
5.25	24

From the results (Figures 18 - 21) the following conclusions can be drawn:

a) The speed of the reaction seems to vary directly with the molarity of NaOH used.

b) At low NaOH/slurry ratios, the reaction is significantly slowed down (probably due to steric effects). At higher NaOH/slurry ratios, the reaction is independent of amounts of NaOH and slurry used.

c) A suitable set of operating conditions to run the process at would be 3M NaOH, 15:1 NaOH/$LaPO_4$ slurry ratio.

4-6. Effect of Temperature on Reactions

To evaluate the effect of higher temperatures on reaction kinetics, the alkali-$LaPO_4$ and lime-alkali reactions were run at 90°C.

Procedure:

The reagents were magnetically stirred as before, and at the same time heated to keep the temperature at about 90°C.

Results:

From Figures 22-24, it is apparent that the effect of temperature

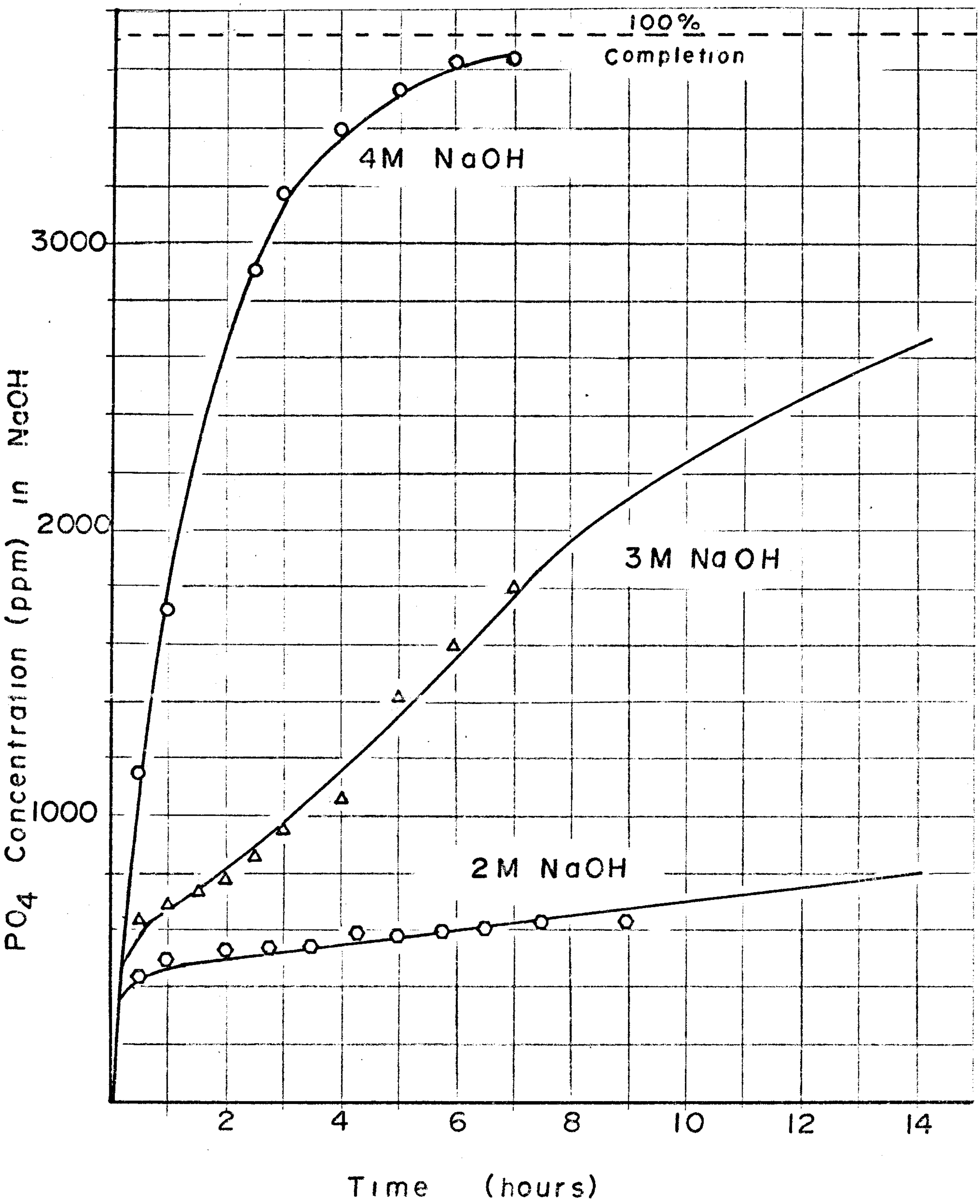

Figure 18 - Kinetic study-NaOH-$LaPO_4$ reaction
NaOH/$LaPO_4$ slurry volumetric ratio = 6.5:1,
initial NaOH molarities as indicated

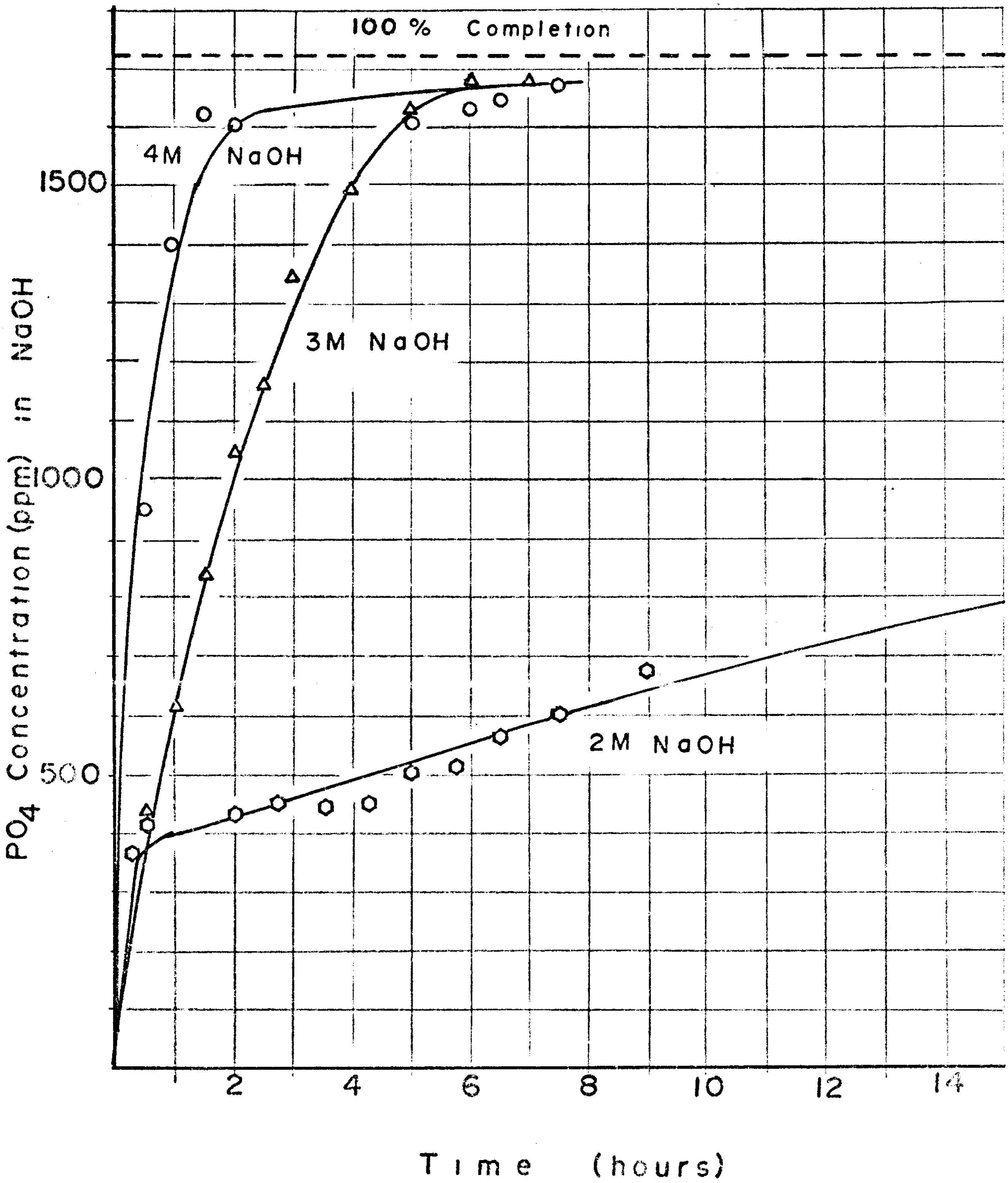

Figure 19 - Kinetic study-NaOH-LaPO$_4$ reaction NaOH/LaPO$_4$ slurry volumetric ratio = 15:1, initial NaOH molarities as indicated

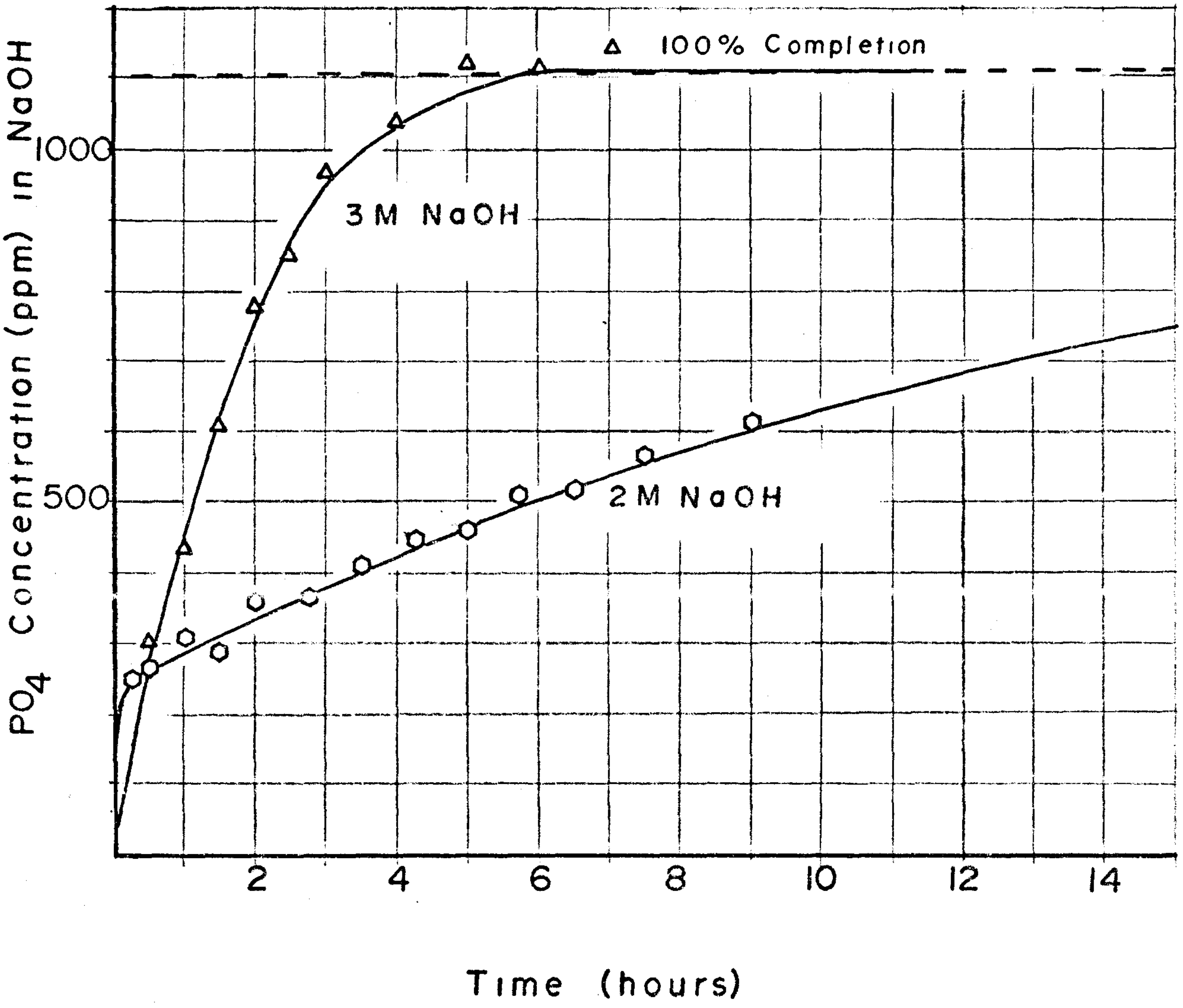

Figure 20 - Kinetic study NaOH-$LaPO_4$ reaction
$NaOH/LaPO_4$ slurry volumetric ratio = 25:1,
initial NaOH molarities as indicated

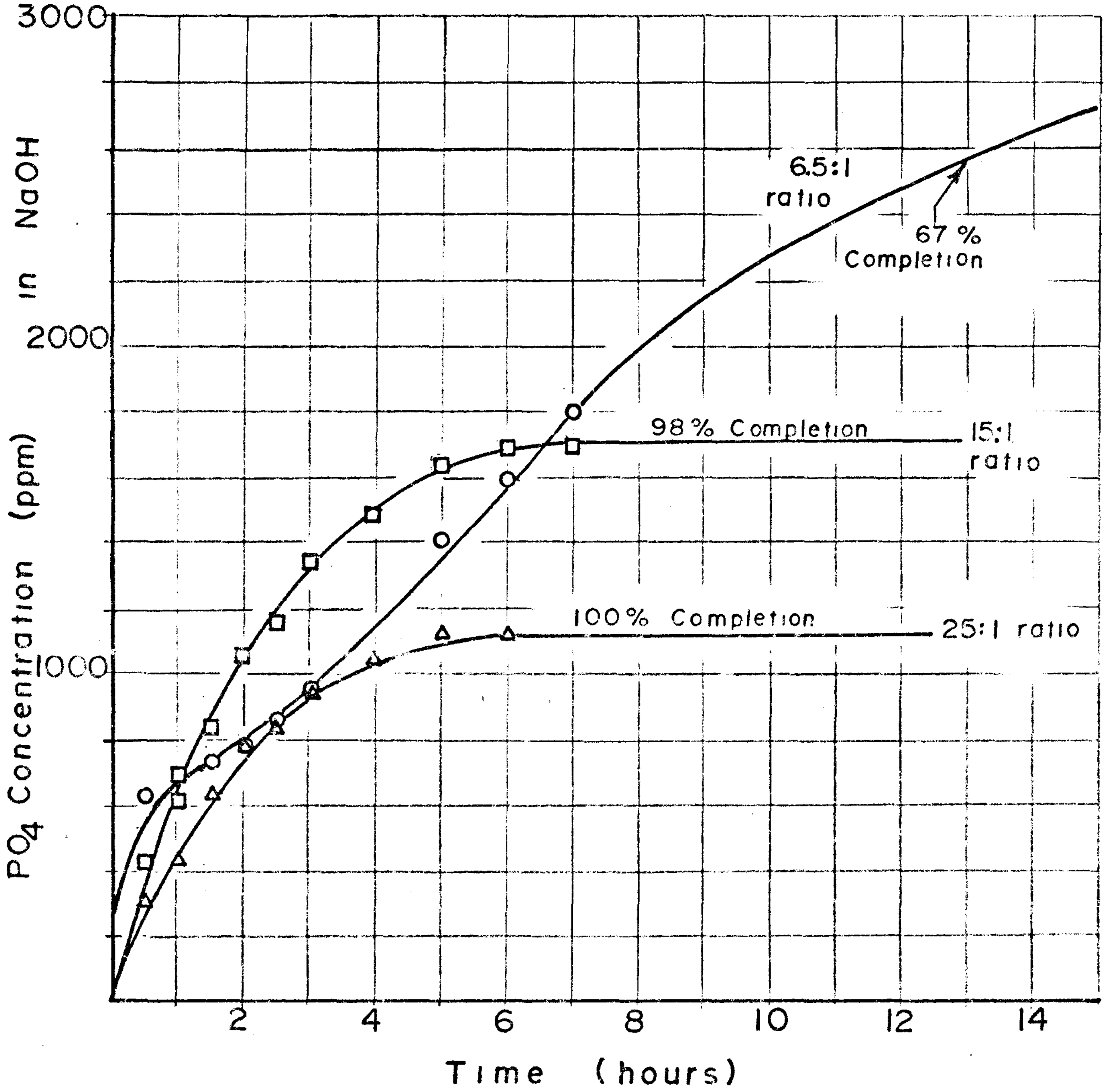

Figure 21 - Kinetic study NaOH-$LaPO_4$ reaction NaOH/$LaPO_4$ slurry volumetric ratio as indicated with 3M NaOH used

TABLE 11

Kinetic Studies of $LaPO_4$-NaOH Reaction - 2M NaOH

Time (hours)	Phosphate Concentration (ppm)		
	NaOH/Slurry Ratio		
	6.5	15	25
0	0	0	0
0.25	440	370	260
0.5	440	420	270
1.0	500		310
1.5			290
2.0	515	430	360
2.75	530	450	370
3.5	535	440	410
4.25	580	450	450
5.0	580	500	460
5.75	590	510	510
6.5	600	560	520
7.5	625	600	570
9.0	635	680	615
22.0	925	925	800
24.0	970	950	810
48.0		1240	970
72.0	1650	1240	950
Phosphate Conc. for 100% Completion	3690	1715	1055

TABLE 12

Kinetic Studies of $LaPO_4$-NaOH Reactions - 3M NaOH

Time (hours)	Phosphate Concentration (ppm)		
	NaOH/Slurry Ratio		
	6.5	15	25
0	0	0	0
0.5	635	435	305
1.0	690	620	440
1.5	730	840	615
2.0	780	1050	780
2.5	860	1160	850
3.0	950	1350	970
4.0	1060	1490	1040
5.0	1410	1630	1100
6.0	1600	1680	1100
7.0	1800	1680	1100
25.0	3200	1720	1100
Phosphate Conc. for 100% Completion	3730	1750	1100

TABLE 13

Kinetic Studies of $LaPO_4$-NaOH Reactions - 4M NaOH

Time	Phosphate Concentration (ppm)	
	NaOH/Slurry Ratio	
	6.5:1	15:1
0	0	0
0.5	1150	950
1.0	1720	1400
1.5		1620
2.0		1600
2.5	2900	
2.75		1600
3.0	3170	
3.5		1600
4.0	3400	
4.25		1600
5.0	3540	1600
5.75		1630
6.0	3620	
6.5		1640
7.0	3630	
7.5		1670
Phosphate Conc. for 100% Completion	3730	1715

is to significantly speed up the kinetics of the reactions (as is to be expected from Arhenius theory of kinetics).

The results show that while the 3M NaOH-$LaPO_4$ reaction is significantly speeded up (close to completion in less than 1/2 hour) the 2M NaOH-$LaPO_4$ reaction is still relatively slow.

Similarly, the lime-alkali reaction for phosphate removal is complete in less than 1/2 hour. (In the run shown, no excess of lime was used.)

4-7. Effect of Phosphate Residual in Alkali

When a stoichiometric (10:6 molar) ratio of $Ca(OH)_2$ to PO_4 is used for phosphate removal from alkali, there remains a phosphate residual in the alkali (see Figure 16).

Since the alkali will be recirculated to react with $LaPO_4$, it is important to evaluate the effect of this PO_4 residual on the NaOH-PO_4 reaction.

An experiment was carried out, with the procedure the same as for $LaPO_4$-NaOH reactions, except that the NaOH used had 550 ppm PO_4 at the start of the run.

From the results in Figure 25, it can be concluded that a lime excess is necessary for complete phosphate removal from the alkali since a phosphate residual would significantly slow down and reduce the yield of the $LaPO_4$-NaOH reaction.

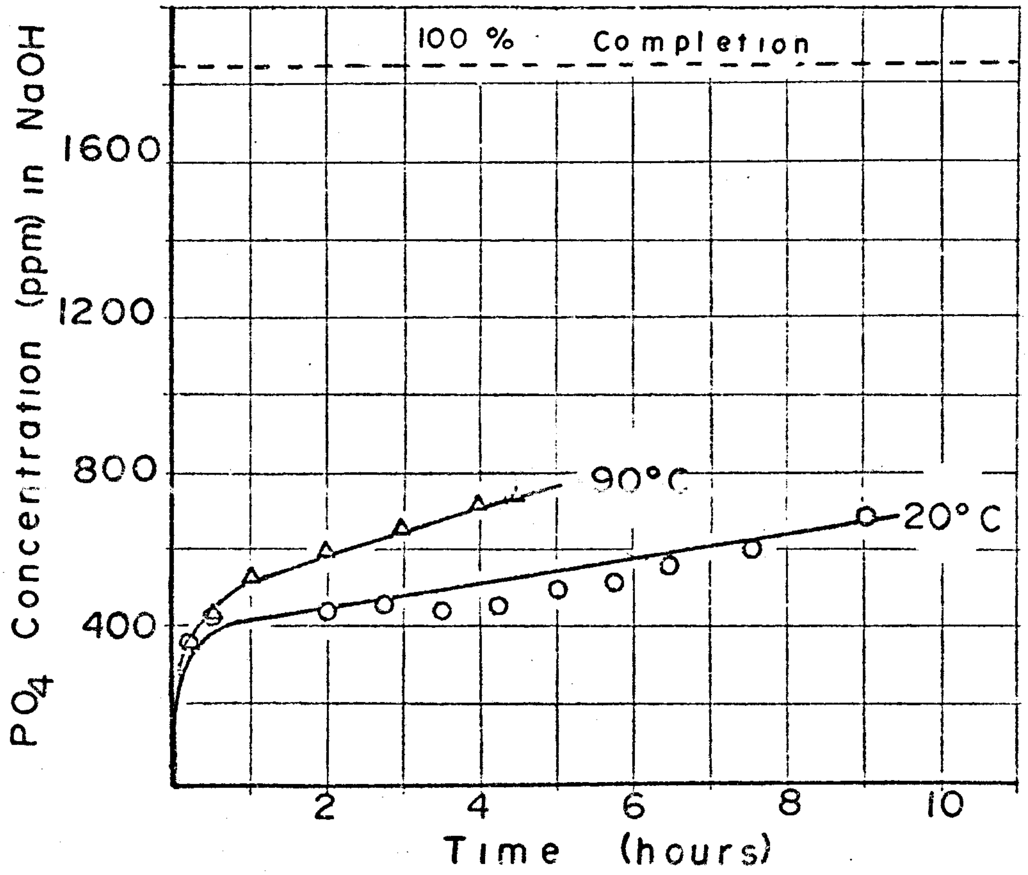

Figure 22 - Effect of temperature on NaOH-$LaPO_4$ reaction NaOH/$LaPO_4$ slurry volumetric ratio = 15:1, with 2M NaOH used

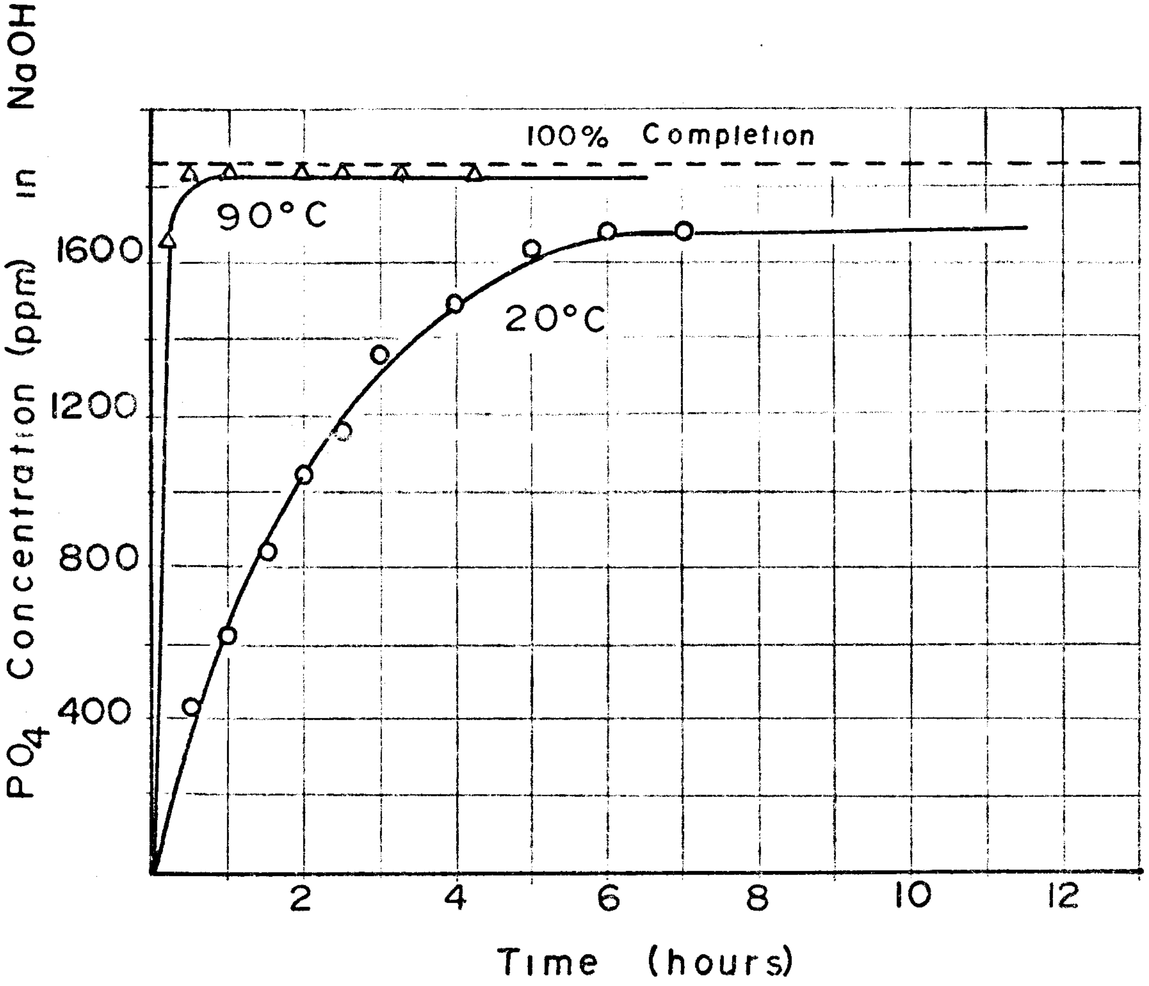

Figure 23 - Effect of temperature on NaOH-$LaPO_4$ reaction NaOH/$LaPO_4$ slurry volumetric ratio = 15:1, with 3M NaOH used

TABLE 14

NaOH-LaPO$_4$ Reaction: Effect of Temperature

14-A - 2M, NaOH/slurry vol. ratio = 15:1; T = 90°C.

Time (hrs.)	(PO$_4$) in Alkali (ppm)
0	
0.25	370
0.5	430
1.0	520
2.0	600
3.0	660
4.0	720
5.0	740
PO4 conc. for 100% completion	1840

14-B - 3M, NaOH/slurry vol. ratio = 15:1; T = 90°C.

Time (hrs.)	(PO$_4$) in Alkali (ppm)
0	
0.25	1650
0.5	1830
1.0	1830
1.5	1830
2.0	1830
2.5	1830
3.25	1830
4.25	1830
PO4 conc. for 100% completion	1840

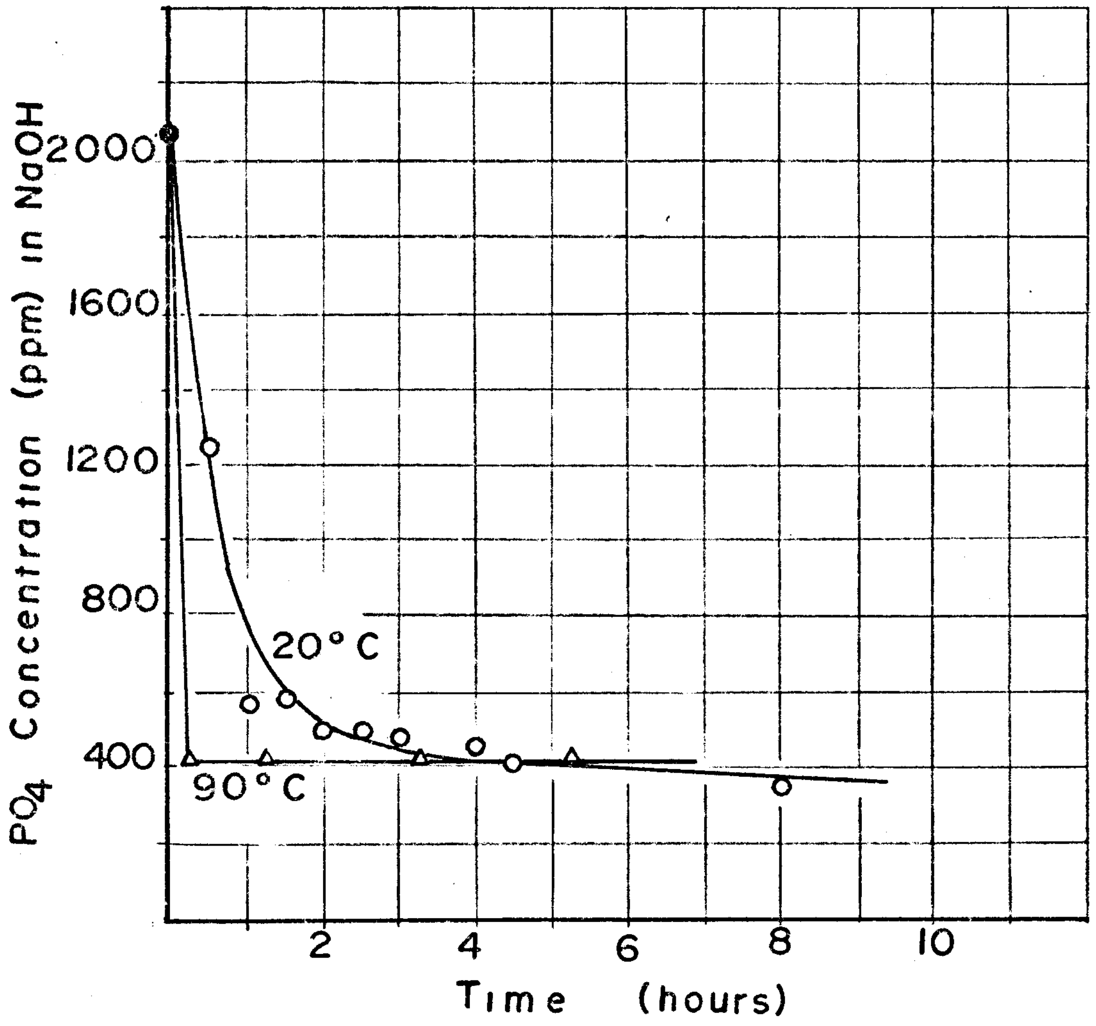

Figure 24 - Effect of temperature on removal of PO_4 with $Ca(OH)_2$

$Ca:PO_4$ molar ratio = 10:6, 3M NaOH

TABLE 15

Phosphate Removal with $Ca(OH)_2$ - Effect of Temperature

10:6 $Ca(OH)_2:PO_4$ Molar Ratio, 90°C, 3M NaOH

Time (hrs.)	PO_4 Concentration in NaOH (ppm)
0	2100
0.25	430
1.25	425
3.25	415
5.25	415

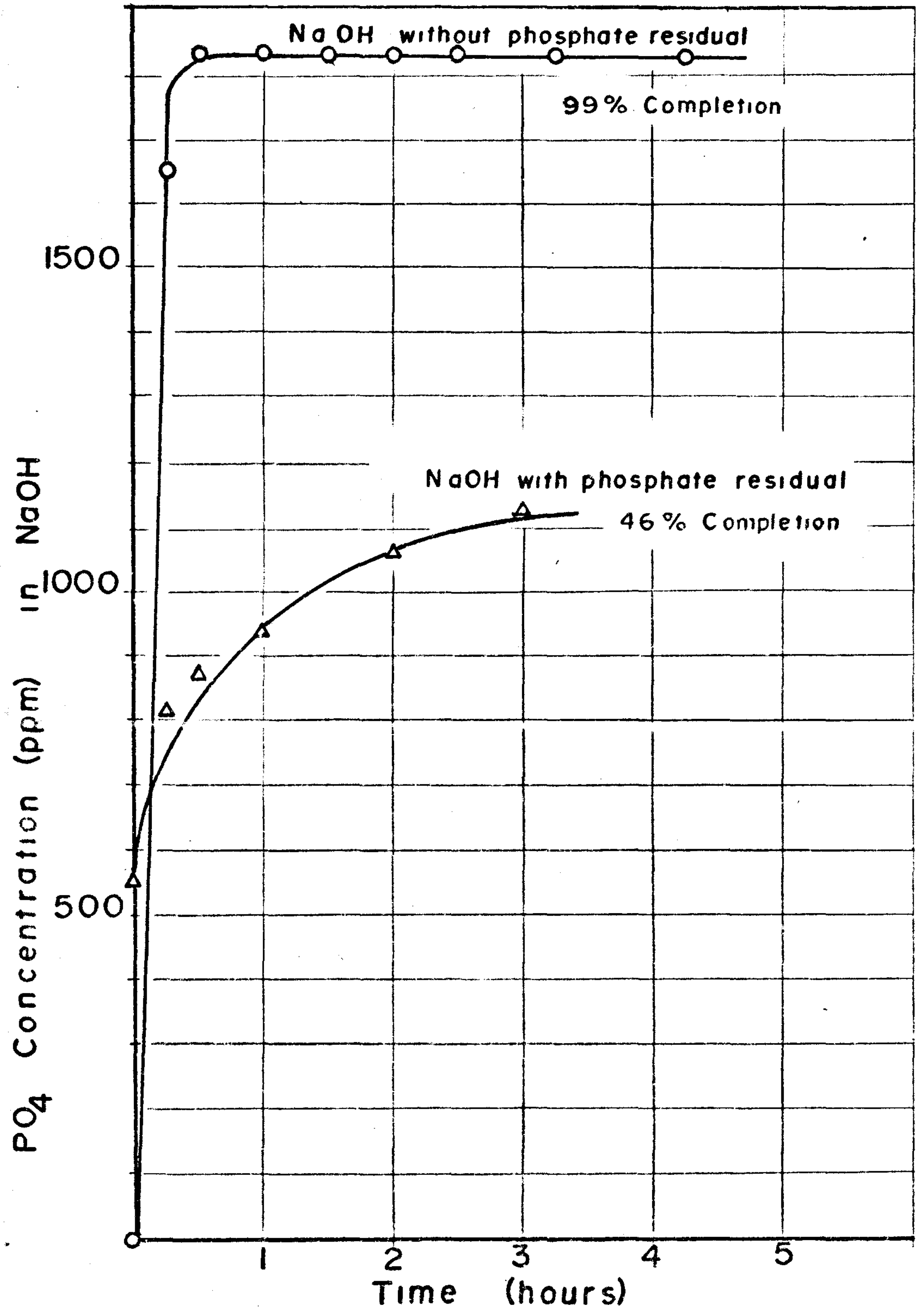

Figure 25 - Effect of phosphate residual on NaOH-$LaPO_4$ reaction NaOH/$LaPO_4$ slurry volumetric ratio = 15:1, 3M NaOH used @90°C

TABLE 16

NaOH-LaPO$_4$ Reaction - Effect of PO$_4$ Residual

NaOH:LaPO$_4$ Slurry Ratio = 15:1 by volume, temperature = 90^{o}C, 3M NaOH

Time (hrs.)	(PO$_4$) in NaOH (ppm)
0	550
0.25	813
0.5	875
1.0	936
2.0	1060
3.0	1125
10.0	1125
(PO$_4$) for 100% completion	2470

4-8. Lanthanum Carryover into Alkali

To determine if there is any lanthanum carryover in the alkali following the NaOH-$LaPO_4$ reaction, lanthanum determinations were performed. From the results in Table 17, it can be seen that there is essentially negligible carryover of La into the alkali, and, furthermore, the lanthanum which does come in is not precipitated by lime, and thus is recirculated. In effect, there is no loss of lanthanum in the regeneration process.

4-9. Lanthanum Recovery

The alkali-$LaPO_4$ reaction yielded products in two phases -- PO_4 dissolved in alkali, and a solid precipitate, mostly $La(OH)_3$. To separate the two, the Lourdes centrifuge was used, at the same operating conditions as before (1/2 hour of spinning at 6000 RPM).

The solids separated were much more concentrated than those obtained when the settled $LaPO_4$ was centrifuged. A solids determination on a sample showed the solids content to be 48.6%.

An attempt to dissolve the solids in distilled water and in secondary effluent was not successful. Tests were therefore conducted to determine the amount of acid required to dissolve the solids.

TABLE 17

Lanthanum Concentrations at Some Process Locations

	La (ppm)
Before NaOH-$LaPO_4$ reaction, concentration as $LaPO_4$.	2600.0
Concentration in alkali following NaOH-$LaPO_4$ reaction.	0.2
Concentration in alkali following lime-PO_4 precipitation.	0.2

Procedure:

A weighted amount of centrifuged solids was placed into a beaker with 100 ml of distilled water. This was magnetically stirred, while acid was added dropwise, till complete dissolution of solids occurred. The total amount of acid added was recorded.

Results:

Millequivalents $La(OH)_3$ in sample	Millequivalents NaOH in sample	Total Millequivalents	Millequivalents of acid used for dissolution
2.58	0.396	2.98	3.25 of H_2SO_4
1.07	0.165	1.24	1.3 of HCl

From these results it can be concluded that a 10% excess of acid (whether HCl or H_2SO_4) over that needed stoichiometrically would suffice to dissolve $La(OH)_3$, and thus complete the regeneration process. (The acid is used up in two reactions - neutralization of NaOH, and dissolution of $La(OH)_3$.)

CHAPTER V

PHASE II - SECONDARY EFFLUENT EXPERIMENTS

5-1. Preliminary Experiments

The work described so far has been with distilled water, to which phosphate has been added. Secondary effluent is, as is to be expected, more complex from the chemical sense. Besides phosphates (condensed and hydrolyzed), it contains carbonates, various organics, and other components, many of which will precipitate lanthanum. In fact, as mentioned previously, Recht et al.(13) have reported no lanthanum in filtrate when an excess of La (2:1 La/PO_4 ratio) was used for phosphate precipitation from secondary effluent, thus indicating complete La precipitation.

In this study, secondary effluent from the Dundas Sewage Treatment Plant was used. Some preliminary tests (Table 18) show that both TOC and phosphate reductions occur on addition of lanthanum to secondary effluent.

5-1-1. Precipitation of Phosphates

To obtain lanthanum phosphate precipitate for the alkali-$LaPO_4$ reaction, the following procedure was used. 20 l of secondary effluent which had been filtered through glass wool were poured into the settling

TABLE 18

Effect of Lanthanum Addition to Secondary Effluent

Amount of La Addition to Secondary Effluent	TOC(ppm)	(PO_4) ppm Residual
Nil	91	12.2
0.7:1 La:PO_4 (Molar Ratio)	71	3.0
1.15:1 La:PO_4	69	0.2
2:1 La:PO_4		< 0.1

tank. The PO_4^{-3} concentration was previously determined as total phosphates (this determination was done with each batch of effluent brought in because of wide fluctuations in PO_4 levels which occur in secondary effluent) and La was added as $La(NO_3)_3 \cdot 5H_2O$ in a 2:1 La/PO_4 molar ratio. The effluent was rapid mixed for 5 minutes (at 150 RPM) then the mixing rate was slowed down to 50 RPM, and mixing continued at this rate for 20 minutes.

The mixing was stopped, and the precipitate formed allowed to settle for 45 minutes. Then, the phosphate free effluent was drained, and the phosphate precipitate transferred to a flask.

The precipitate formed was different from that formed in distilled water. Whereas the latter was milky white in colour and very fragile, the effluent phosphate precipitate was straw-coloured, and not as fragile. Furthermore, centrifuging of the effluent precipitate at the same operating conditions as before yielded 12% solids instead of the 7% for $LaPO_4$ from distilled water. This centrifuge cake did not flow as the slurry obtained previously did.

A determination showed that the solids precipitated contained 18% PO_4^{-3}, 53% La^{+3}, and 29% of other co-precipitants by weight (see Appendix V for sample calculation).

5-2. Regeneration Reactions

5-2-1. Alkali Reaction with Lanthanum Precipitate

Procedure:

To 10 gms of centifuged $LaPO_4$ solids, 150 ml. of 3M NaOH were added. The reagents were stirred magnetically, and kept at 90°C.

Results:

Figure 26 shows 88% reaction completion within about 1/2 hour reaction time. The alkali changed in colour during the reaction from colourless to deep straw colour. This change was probably due to organics from secondary effluent.

Centrifuging (at 6000 RPM for 1/2 hour) the products of the reaction yielded a centrifuge cake containing 37% solids. Appendix VI shows typical cake composition. The liquid phase alkali with phosphate was then reacted with lime for phosphate precipitation.

5-2-2. Phosphate Precipitation from Alkali

Procedure:

An excess of lime ($Ca:PO_4$ = 20:6 molar ratio) was added to the alkali. The reagents were stirred magnetically, and kept at 90°C.

Results:

Figure 27 shows 97% phosphate removal in less than 1/2 hour reaction time.

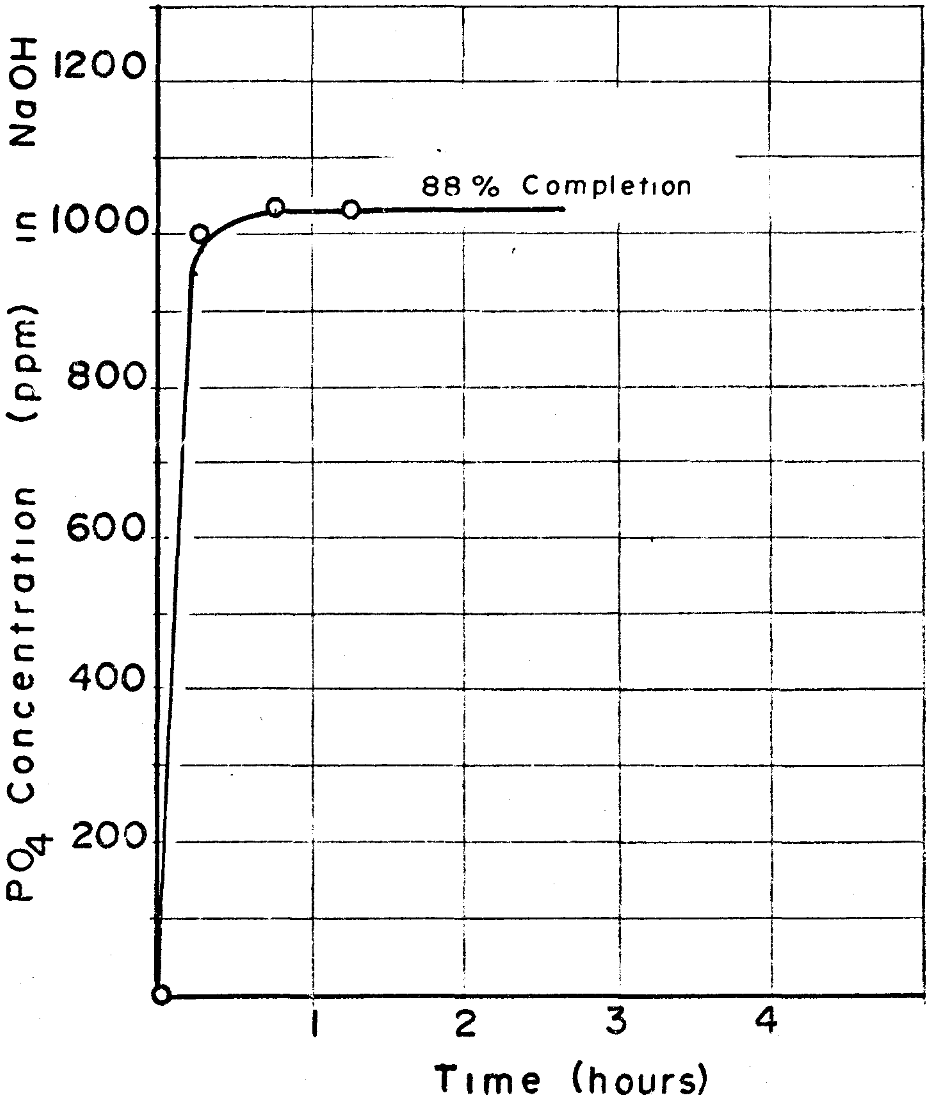

Figure 26 - Secondary effluent experiments

$LaPO_4$-NaOH reaction

3M NaOH used at 90°C

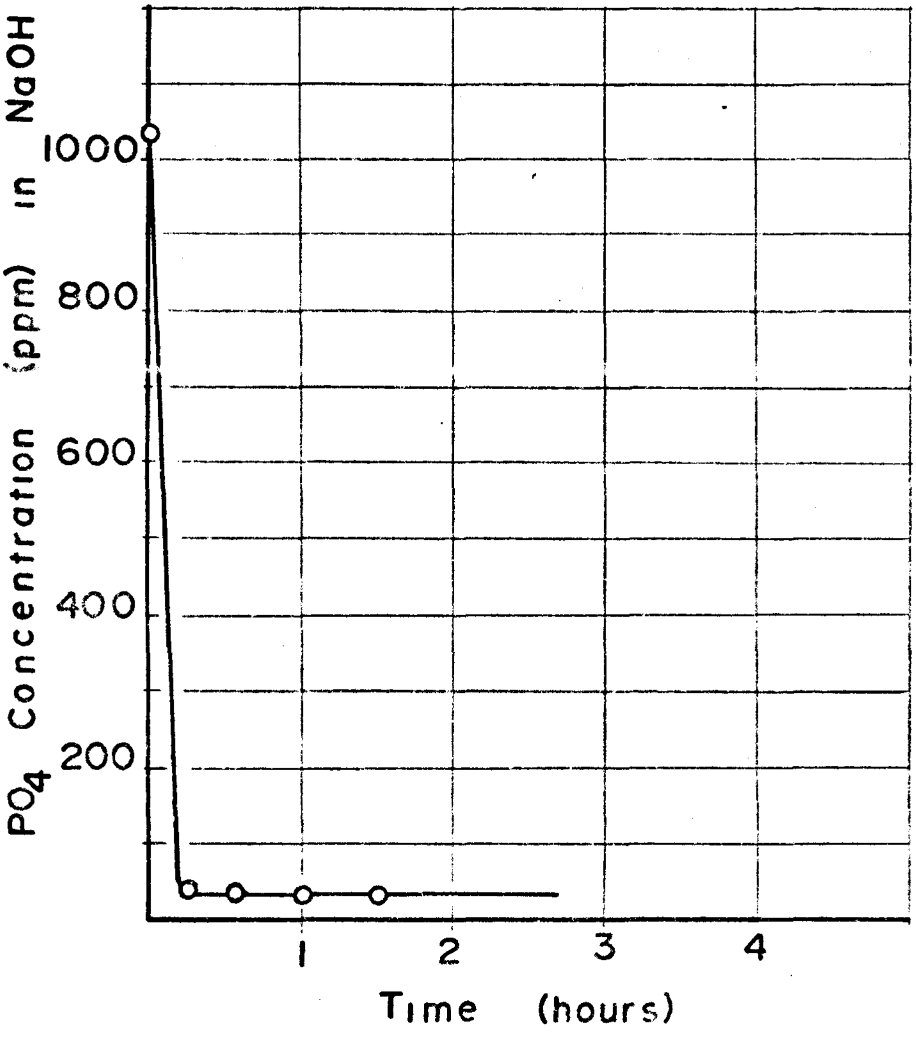

Figure 27 - Secondary effluent experiments

Removal of phosphates from NaOH

Ca:PO$_4$ molar ratio = 20:6 (excess of Ca(OH)$_2$

used), temperature 90°C.

TABLE 19

$LaPO_4$-3N NaOH Reaction (Secondary Effluent)

Time (hours)	(PO_4) in NaOH (ppm)
0	0
0.25	1010
0.75	1035
1.25	1035
(PO_4) for 100% completion	1150

TABLE 20

Lime-PO_4 Reaction (Secondary Effluent)

Time (hours)	(PO_4) in NaOH (ppm)
0	1030
0.25	40
0.50	35
1.0	30
1.5	30

5-2-3. Lanthanum Recovery

A weighed sample of centrifuged $La(OH)_3$ precipitate cake was placed into a beaker, with 100 ml of distilled water. This was magnetically stirred, while acid was added dropwise, till complete dissolution of solids occurred. The total amount of acid added was recorded.

Results:

Weight of precipitate cake	1.5628 gm
Ml of H_2SO_4 acid used	1.35 ml

(Weight of acid used = 1.35 ml $\div$ 1.8 gm/ml (Sp.gr. of H_2SO_4)

= .75 gms.)

5-3. Lanthanum Regeneration Schemes

The results of the preceeding sections suggest two possible schemes for a lanthanum regeneration process.

5-3-1. Scheme A

Figure 26 shows the flow sheet of a process for La regeneration. After lanthanum precipitation of phosphates from secondary effluent, the precipitate is settled, then centrifuged to remove excess water. The resulting $LaPO_4$ slurry is reacted with hot (90°C) 3M NaOH at a NaOH to $LaPO_4$ slurry ratio of 15:1. The La $(OH)_3$ precipitate produced is separated from NaOH, and reacted with H_2SO_4 to resolubilize the lanthanum, which is then recycled for further phosphate precipitation.

The still hot alkali stream, now diluted, and containing PO_4 in solution is then broughtin contact with an excess of lime in a second reactor. Phosphates are precipitated out, and phosphate free NaOH is passed on to an evaporator to remove water picked up in reactor #1 from the $LaPO_4$ slurry. Following evaporation of excess water, anhydrous NaOH is added to make up

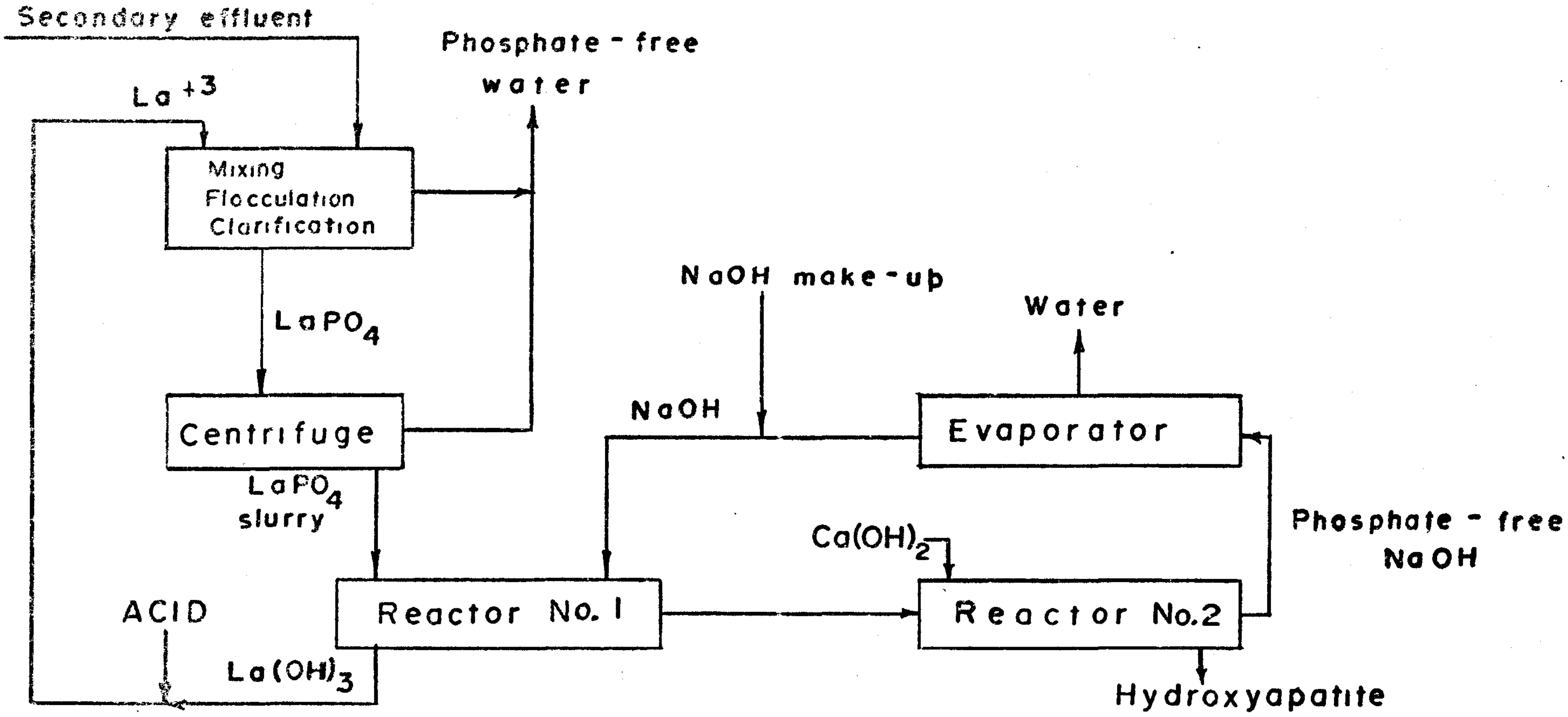

Figure 28 - Lanthanum recovery- Scheme A

losses of NaOH. The NaOH is then recycled to reactor #1.

5-3-2. Scheme B

The results of section 4-4-3 suggest the regeneration scheme shown in figure 29. Following reaction between $LaPO_4$ slurry and 6M NaOH, the alkali stream containing phosphates is cooled in a crystallizer to -17°C. Phosphates crystallize out as a sodium-phosphate compound, and the phosphate-free alkali passes on to an evaporator. As in the previous scheme, the $La(OH)_3$ produced in reactor #1 is dissolved with acid, and recycled for phosphate precipitation.

5-4. Economic Comparison

Since a cost evaluation (Appendix 7) showed scheme A would be less costly to operate, process design calculations were carried out using this scheme (Appendix 8) to obtain order of magnitude figures for amounts and costs of chemicals required and amounts of sludge produced. Table 21 summarizes these values.

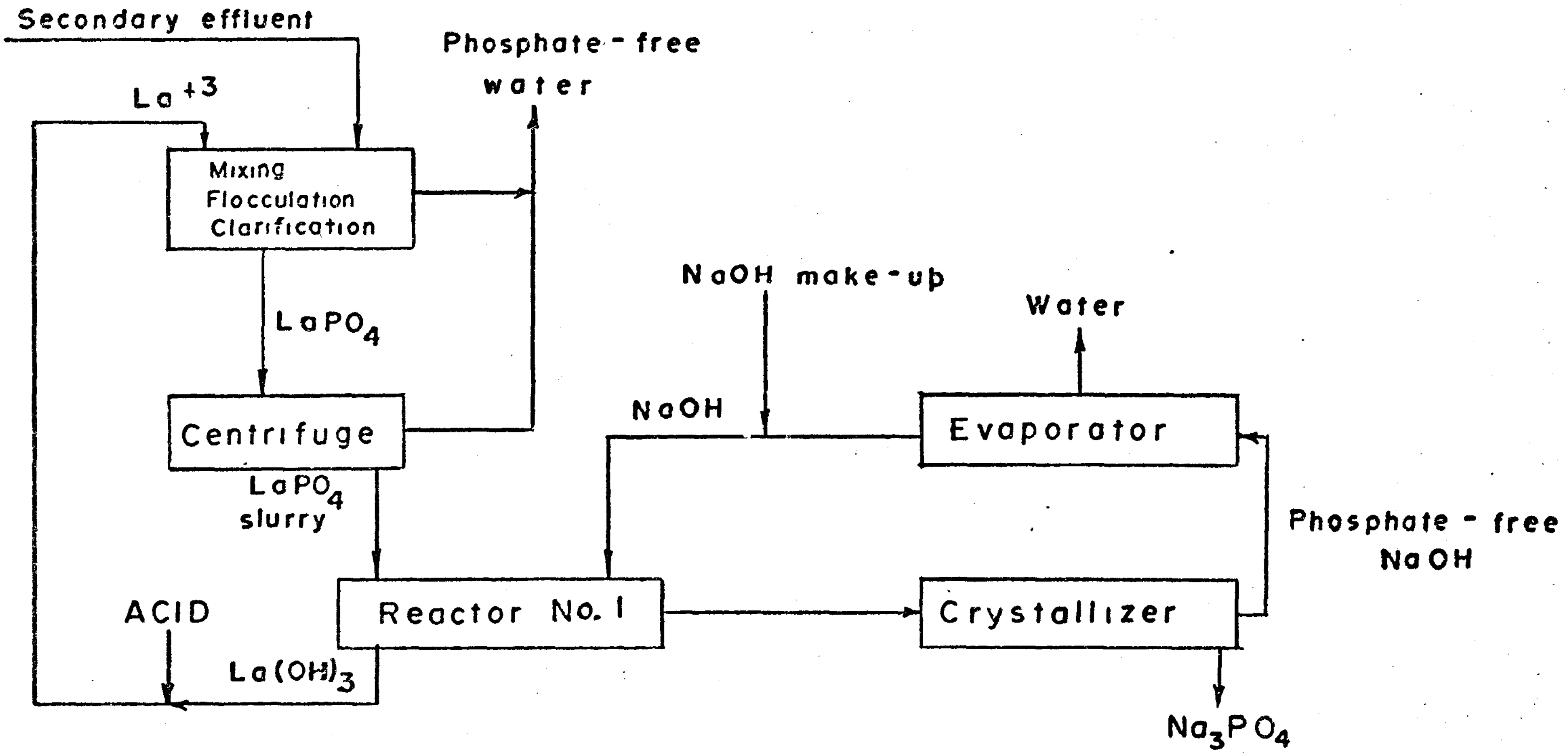

Figure 29 - Lanthanum recovery - Scheme B

Table 21 - Process estimates for regeneration of lanthanum following precipitation of phosphates from waste-waters, based on a 1 million gallon flow of waste-water.

AMOUNT OF CHEMICALS AND FUEL REQUIRED	158.4 lbs (72 kg) NaOH 1078 lbs (490 kg) H_2SO_4 462 lbs (210 kg) $Ca(OH)_2$ 70.5 gallons fuel oil.
CHEMICAL AND FUEL COST	$70
AMOUNT OF EXTRA SLUDGE PRODUCED	528 lbs (240 kg)

CHAPTER VI

CONCLUSIONS

Regeneration of lanthanum following precipitation of phosphates from waste-water is technically feasible. Process design calculations indicate a chemical and fuel cost of approximately $70 per million gallons of waste-water treated.

Chemical reactions for regeneration of lanthanum following precipitation of phosphates from water depend on molar strength of alkali and ratios of reagents used.

Temperature has a significant effect on regeneration reaction kinetics.

By proper selection of temperature, ratio of reagents, and molar strength of alkali, almost total reaction completion takes place within 30 minutes for $LaPO_4$ -- alkali reaction, and lime-phosphate precipitation.

Satisfactory separation of reacted reagents is achieved by centrifuging.

An economic comparison indicates that precipitation of phosphates from alkali with lime is cheaper than phosphate removal by crystallization.

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APPENDIX 1

SOLIDS DETERMINATION OF FLOC:

Procedure: 20 ml of settled $LaPO_4$ precipitate were transferred by pipette to pre-weighed micro-pore filters. Vacuuming removed most of the water, with the remainder evaporated in a 103°C oven.

Weighing of the dried sample and filter then allowed the computation of solids in floc.

Sample calculation:

Weight of filter:	1.5598 gms.
Weight of dry filter and precipitate:	1.5993 gms.
Weight of precipitate:	.0395 gms/20 ml

Therefore, solids concentration is: 1.975 gms/ℓ

≈ 1975 ppm

APPENDIX 2

SOLIDS DETERMINATION OF $LaPO_4$ SLURRY:

Procedure: 2 ml specific gravity bottles were used. The pre-weighed bottle was filled with slurry, and weighed. It was then placed in a 103° oven overnight, and the slurry dried. The bottle with the $LaPO_4$ crystals was then weighed, and from the values obtained, the density, and solids concentration of the slurry determined.

Sample calculation:

Weight of empty bottle:	8.6274 gms.
Weight of bottle and slurry:	10.7754 gms.
Weight of bottle and crystals:	8.7580 gms.

Slurry density: $\frac{(10.7754 \text{ gm} - 8.6274 \text{ gm})}{2 \text{ ml.}} = 1.074$ gm/ml.

Solids concentration: $\frac{(8.7580 \text{ gm} - 8.6274 \text{ gm})}{2 \text{ ml}} = 0.653$ gm/ml

$\approx 65{,}000$ ppm

APPENDIX 3

PHOSPHATE DETERMINATION:

Phosphate determinations were performed on the Technicon Auto-Analyzer - an instrument which provides fast, automated chemical analysis. Since phosphate can exist in several forms - the simplest inorganic orthophosphates, as well as condensed phosphates such as pyrophosphate and polyphosphate - analysis is typically classified as orthophosphate determination, and total phosphate determination. For the latter, all condensed phosphates are hydrolyzed to the simplest orthophosphate.

In Phase I of this study, only orthophosphate determinations were needed. Because some fraction of phosphates in secondary effluent is still in the organic, condensed form, all determinations in Phase II of the study were for total phosphate.

Since the Autoanalyzer range for phosphate detection lies between 0 and 40 ppm, while the samples examined had phosphate concentrations from 0 to 3500, those samples whose phosphate concentrations were above 40 ppm were diluted with distilled water so that detection in the 0 - 40 ppm range could be made. The method of analysis used, and procedures followed are outlined in the instrument manual[21].

APPENDIX 4

LANTHANUM DETERMINATION

Lanthanum determination was performed by a titration technique using the Orion Model 94-09 flouride in activity electrode. The data obtained was plotted on Gran's plot paper - a semi-antilog paper which allows one to obtain straight line titration curves. The procedure followed is outlined in Orion Newsletters[22].

For lenthanum determinations in 3N NaOH, the NaOH solution was neutralized to pH 5 with HCℓ. A blank containing similar concentrations of Na^{+1} and $C\ell^{-1}$ ions was used in the determinations.

APPENDIX 5

DETERMINATION OF COMPONENTS IN $LaPO_4$ SOLIDS CAKE FROM SECONDARY EFFLUENT:

A phosphate determination of secondary effluent gave a PO_4 concentration of 16 mg/ℓ.

To 20 ℓ of secondary effluent, 2.78 gms of $La(NO_3)_3 \cdot 5 H_2O$ was added (a 2:1 La:PO_4 molar ratio). The .66ℓ of sludge formed as a result of the precipitation were collected, and a solids determination gave the solids contents of the sludge as 2660 mg/ℓ. Since a phosphate determination of the decanted effluent showed no PO_4 remaining, it can be safely assumed that the sludge contains all of the PO_4.

Therefore $20\ell \times 16\ \text{mg}/\ell = .66\ell \times [PO_4]$

Concentration of PO_4 = 485 mg/ℓ

Since all the lanthanum also is precipitated (as shown by Recht et al(13)), and a 2:1 La:PO_4 molar ratio was used, concentration of lanthanum is floc is

$$485 \times 2 \times \frac{138.91}{95} \quad \frac{(\text{M.W. of La})}{(\text{M.W. of } PO_4)} = 1410\ \text{mg}/\ell$$

Therefore solids content of precipitate by weight is

18% PO_4

53% La

29% other precipitates

APPENDIX 6

DETERMINATION OF COMPONENTS IN $La(OH)_3$ SOLIDS CAKE

The products of the $LaPO_4$ - NaOH reaction (lanthanum phosphate precipitated from secondary effluent) were centrifuged. A determination of a 1.56 gm cake sample showed it to contain 56.6% water, 7.05% NaOH, and 36.3% solids by weight. The cake was thus dissolved in acid, and a phosphate determination showed that it had contained 16.6 mg PO_4. Since the $LaPO_4$ - NaOH reaction was 88% complete (figure 28), this represented 12% of the unreacted phosphates. Thus, the composition of cake is:

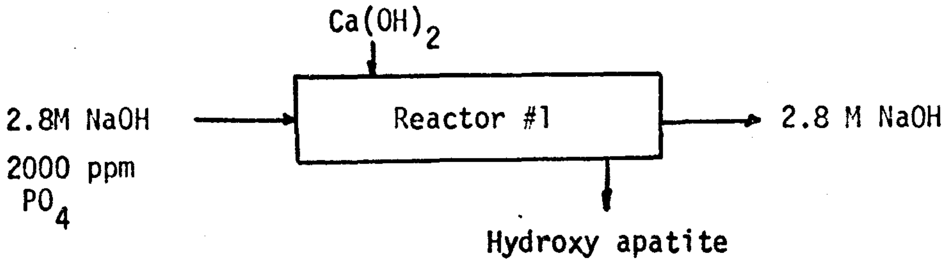
56.6% water
7.05% NaOH
1.06% PO_4
35.3% ($La(OH)_3$ and other solids)

APPENDIX 7

COST COMPARISON OF TWO METHODS OF PRECIPITATION OF PHOSPHATES FORM NaOH:

As mentioned above (sections 4-4-3 and 4-4-4), two methods of precipitating phosphates from NaOH were found. The following is a cost comparison on a basis of 100 ℓ/min. alkali flow.

Method A:



100 ℓ of alkali contains

$$100\ \ell \times 2000\ \text{mg}/\ell\ \text{PO}_4 = 200\ \text{gm PO}_4$$

Amount of lime required to precipitate this phosphate is:

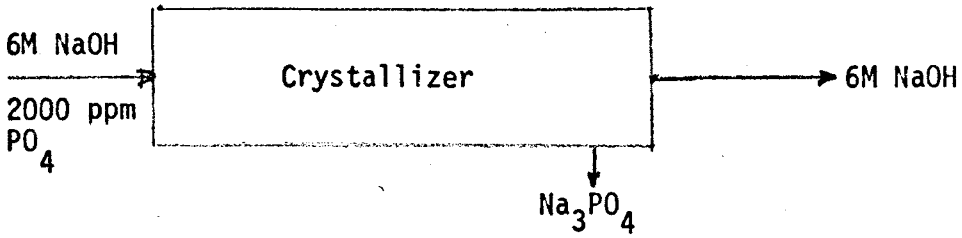
(assuming use of excess lime):

$$200\ \text{gm} \times \frac{20}{6}\ (\text{Ca:PO}_4\ \text{molar ratio}) \times \frac{79.08}{95.04}\ \frac{(\text{Molecular weight})(\text{Ca(OH)}_2)}{(\text{Molecular weight PO}_4)}$$

$$= 520\ \text{gms Ca(OH)}_2$$

at current price of 3¢/lbs. this costs 3.4¢/100ℓ of NaOH.

Method B:



Assuming the stream enters the crystallizer at 90°C, the precipitation of phosphate is brought about by lowering the temperature of alkali to -17 C.

Energy is required here for two operations:

A) Lower the temperature of the alkali to -17°C.

B) After crystallization, raise the temperature of the alkali to 90°C.

For step B, energy required (for 100ℓ of alkali) is:

1.108 kg/ℓ x .81 Kcal/kg°C x 100ℓ x (90° - (-17°)

Density x Specific Heat x Volume x Change in Temperature

= 9600 Kcal/min.

= 38,400 Btu/min

Since fuel oil has heat value of 135,000 Btu per gallon, .28 gallons will be required per min. At current fuel oil prices of 20¢ /gallon, this costs 6¢/ 100ℓ of NaOH.

Further to this, refrigeration required in step B will further boost this cost.

Thus, scheme A appears the more economical one to use.

APPENDIX 8

PROCESS DESIGN EXAMPLE:

The flowsheet of scheme A is used here to obtain order of magnitude figures for amounts of chemicals required, amounts of sludge produced, and reactor sizes, assuming a 1MGD flow of secondary effluent containing 20 ppm PO_4.

N.B. Total recovery of lanthanum precipitate for regeneration is assumed.

PHOSPHATE INPUT:

$$1{,}000{,}000 \text{ gal} \times 20 \text{ mg } PO_4/\ell \times 4.54\ \ell/\text{gal} = 90.8 \text{ kg } PO_4$$

LANTHANUM REQUIRED:

At 2:1 La: PO_4 ratio,

$$90.8 \text{ kg } PO_4 \times \frac{138.91}{95.04}\ \frac{(\text{Molecular weight La})}{(\text{Molecular weight } PO_4)} \times 2 = 264 \text{ kg La}$$

INPUT INTO REACTOR #1

From batch experiments, it was found that the centrifuge cake produced from $LaPO_4$ precipitate contained 12% solids. These solids in turn contained 18% PO_4 (all percentages by weight). Assuming precipitation of phosphates, separation of $LaPO_4$ precipitate, and PO_4 content in centrifuge cake is as obtained in batch experiments, amount of $LaPO_4$ cake produced

$$= 90.8 \text{ kg } PO_4 \times \frac{1}{18\%\ PO_4 \text{ in cake solids}} \times \frac{1}{12\% \text{ solids in cake}}$$

= 4200 kg of centrifuge cake. 9240#

Using 15ℓ of 3M NaOH per kg of cake, amount of 3M NaOH required is:

$$4200 \text{ kg} \times 15\ \ell/\text{kg} = 63{,}000\ \ell \text{ 3M NaOH}$$

PRODUCTS FROM REACTOR #1

Taking conversion of $LaPO_4$ to $La(OH)_3$ in reactor #1 at 88% and same separation of $La(OH)_3$ precipitate from alkali as obtained in batch experiments, the composition of $La(OH)_3$ cake produced is (see Appendix 6)

56.6% water
7.05% NaOH
1.06% PO_4
35.3% $La(OH)_3$ and other solids.

Of the 90.8 kg PO_4 in $LaPO_4$ cake, 12% (10.8 kg) remains unreacted, and is carried over in the $La(OH)_3$ cake. But 1.06% of cake weight was found to be PO_4. Therefore, weight of cake produced is:

$$\frac{10.8}{.0106} = 1020 \text{ kg of } La(OH)_3 \text{ cake.}$$

Furthermore, weight of NaOH in cake, and which has to be made up later in the process is:

$$1020 \text{ kg} \times 7.05\% = 72 \text{ kg}$$

Since amount of H_2SO_4 acid required to redissolve the $La(OH)_3$ centrifuge cake was .75 gms. per 1.56 gms of cake (section 5-2-3), weight of acid required is:

$$1020 \text{ kg} \times \frac{.75}{1.56} = 490 \text{ kg.}$$

The $LaPO_4$ centrifuge cake coming into reactor #1 contains 88% water. This causes dilution of NaOH:

$$\frac{63{,}000\ell \text{ 3M NaOH}}{63{,}000\ell \text{ 3M NaOH} + .88 \times 4200 \text{ kg} \times 1\text{kg}/\ell\ H_2O} = 66{,}700\ell \text{ of } 2.82 \text{ M NaOH}$$

Since $La(OH)_3$ cake is made up of 63.6% 2.82 M NaOH, loss of the alkali in this stream is:

$$.636 \times 1080 \text{ kg} \times \frac{1}{1.108 \text{ kg}/\ell \text{ of } 2.82 \text{ M NaOH}} = 625\ell \text{ of } 2.82 \text{ of NaOH}$$

INPUT INTO REACTOR #2:

Volume of NaOH into reactor # 2 is

$66{,}700 - 625 \approx 66{,}000\ell$, containing 90.8 kg $PO_4 \times .88$

$= 80$ kg PO_4

Amount of lime required (using Ca:PO_4 molar ratio of 20:6) is

$$80 \text{ kg } PO_4 \times \frac{20}{6}\frac{(Ca)}{(PO_4)} \times \frac{74.08 \text{ (Molecular Weight } Ca(OH)_2)}{95.04 \text{ (Molecular Weight } PO_4}$$

$= 210$ kg $Ca(OH)_2$

PRODUCTS FROM REACTOR #2:

Products from reactor # 2 will be in two phases - the liquid alkali, now practically phosphate free, and the calcium phosphate (mostly hydroxyapatite) solids. Assuming complete separation of these two phases will be achieved, total weight of solids produced is equal to

A) Weight of phosphate precipitated

\+ B) Weight of $Ca(OH)_2$ added

\- C) Weight of OH^{-1} ions taken up from $Ca(OH)_2$ to replace PO_4^{-3} ions precipitated

$$= 80 \text{ kg } PO_4 + 210 \text{ kg } Ca(OH)_2 - 80 \text{ kg } PO_4 \times \frac{3 \times 17 \text{ (Mol.wt. of OH)}}{95.04 \text{ (Mol. wt. of } PO_4)}$$

$= 236.5$ kg

ALKALI MAKE-UP:

To bring the alkali to strength (from 2.82 M to 3M), water has to be evaporated, and loss of 72 kg of NaOH in $La(OH)_3$ cake made-up. Amount of water to be evaporated

= 66,000ℓ - 63,000ℓ = 3000ℓ

If the alkali stream out of reactor #2 is at 90°C, evaporation of excess water proceeds in two steps.

A) Raise temperature of alkali to boiling point (103° for 2.8M NaOH)

66,000ℓ x (103°C - 90°C) x .81 Kcal/kg°C x 1.108 kg/ℓ = 770,000 Kcal.

Volume x Change in Temperature x Specific Heat x Density

B) Evaporate 3000ℓ of water

3000ℓ x 540 kcal/kg x 1Kg/ℓ = 1,620,000 Kcal.

Volume x Heat of Vaporization x Density

Thus, a total heat load of 2,390,000 K cal results from this operation. Since fuel oil has heat value of 135,000 BTU/gal., amount of oil required is:

$$2{,}390{,}000 \text{ Kcal} \times \frac{1\text{BTU}}{.252 \text{ Kcal}} \times \frac{1 \text{ gal of oil}}{135{,}000 \text{ BTU}} = 70.5 \text{ gallons.}$$

SIZE OF REACTORS:

The results of kinetic experiments carried out (section 5-2-1, 5-2-2) indicate that a retention time of about 1/2 hour for both the NaOH-$LaPO_4$ reaction, and the lime-phosphate precipitation is adequate.

Since the volumetric input is about 70,000ℓ/day, the size of the reactors required is:

$$70{,}000\ell/\text{day} \times \frac{1}{48} \text{ days retention time} = 1460\ell \text{ capacity.}$$