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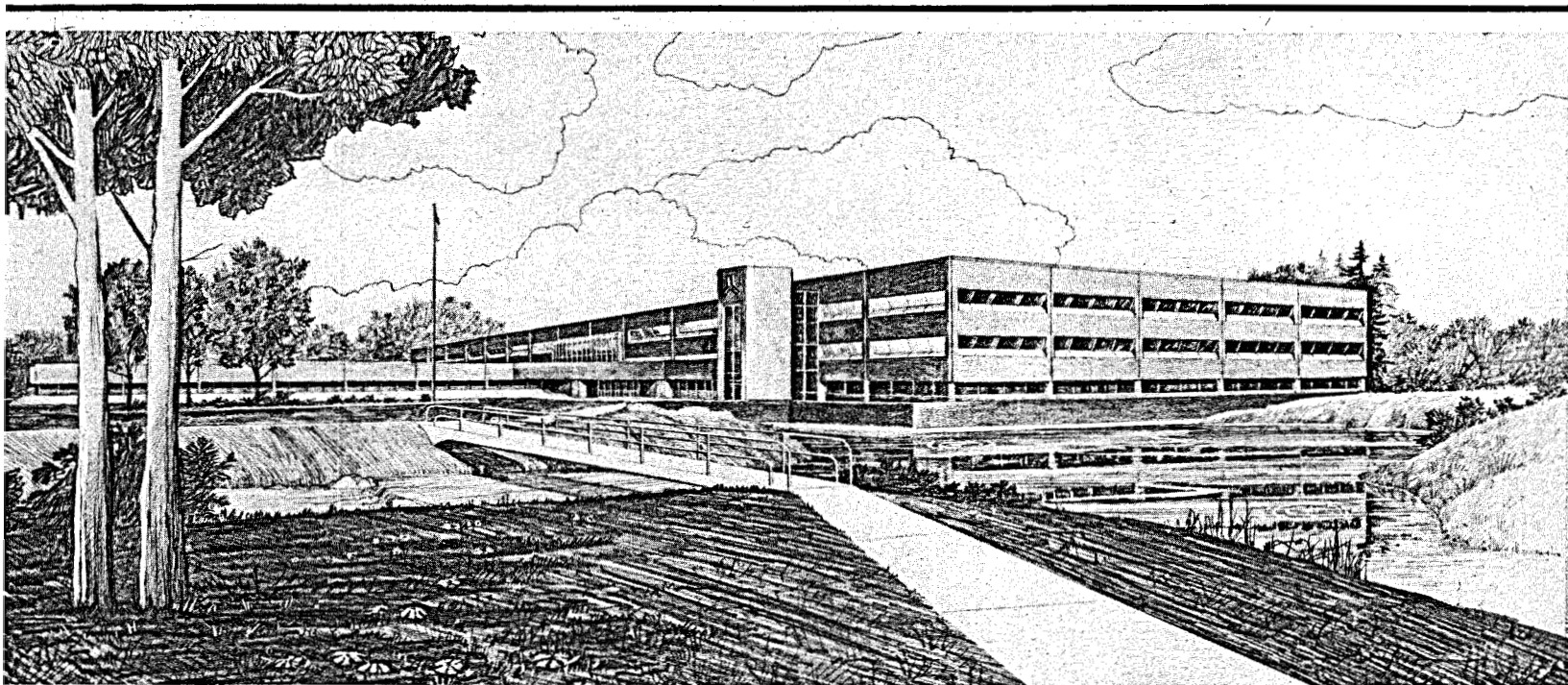
ZETA POTENTIAL STUDY OF THE WATER TREATMENT
OF GEOTHERMAL BRINES

MASTER

P. M. Wikoff

D. F. Suci

U.S. Department of Energy
Idaho Operations Office • Idaho National Engineering Laboratory



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ABSTRACT

Before the cooled geothermal fluid can be used as a coolant in the operation of the 5MW(e) Geothermal Pilot Power Plant, the fluid must be treated to reduce the silica and hardness and to control corrosion. Prior to reinjection, the blowdown must be treated to remove the phosphate (one of the corrosion inhibitors added to the system). The zeta potential study was conducted to study the surface reactions occurring in the flash mixing of the cooled geothermal with magnesium oxide, lime, and polyelectrolyte for silica removal and to determine the optimum polyelectrolyte necessary in the silica reduction system and the reduction of the phosphate in the tower blowdown with ferrous sulfate.

The investigation indicates a bridging type adsorption occurs in the silica reduction system. The proposed mechanism is described. The study indicated that between 150 and 250 ppm of magnesium oxide was necessary to achieve this reduction with one ppm of Betz 1125L. This is a substantial savings over the planned value. Investigation of the phosphate reduction system showed that a cationic polymer was necessary to achieve good flocculation and settling.

SUMMARY

Prior to use as a coolant in the operation of the 5MW(e) Geothermal Pilot Power Plant, the cooled geothermal requires a pretreatment process for silica and hardness reduction and a treatment process for corrosion control. The zeta potential studies reported here were conducted to study the surface reactions occurring in the silica reduction system, and to determine the optimum flocculant concentration required for good silica removal. In addition, the optimum flocculant and flocculant concentration was examined for the phosphate reduction system.

The results of the zeta potential study on the silica reduction system suggests adsorption between the magnesium hydroxide formed in solution and the silica. With the addition of calcium ion, there is a bridging type adsorption between the silica-magnesium hydroxide particles. The optimum MgO concentration, added as $MgCl_2$, is between 150 to 250 ppm of MgO. The optimum pH was 10.2 adjusted with lime. Betz 1125L will be the polymer used. The data indicates 1 ppm will result in the maximum silica reduction. An excess of the polymer, 8 ppm or greater, will result in more silica remaining in solution.

The zeta potential study of the phosphate reduction system indicates that the optimum iron concentration lies between 20 and 30 ppm iron added as ferrous sulfate. Optimum pH is 9.2 adjusted with lime. Betz 1195, cationic polymer produced the largest and best settling flocs. The optimum polymer concentration is 2 to 4 ppm of Betz 1195. The data for the phosphate system was obtained for domestic water without the presence of zinc sulfate or dispersants that will be present in the blowdown water. Further optimization will probably be necessary when operating.

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1.0 INTRODUCTION

Due to the location, the operation of the 5MW(e) Geothermal Pilot Power Plant requires the use of cooled geothermal water as a coolant to circulate between the condenser and the wet (open-loop, evaporative) cooling tower. The system requires a pretreatment process for silica and hardness reduction and a treatment process for corrosion control.

In the pretreatment process, as established by Suciu and Miller¹, the cooled geothermal water is flash mixed with $MgCl_2$ and lime (pH 10.2) for silica removal. Soda ash is added to reduce the hardness. After flash mixing, Betz 1125L (a coagulating aid) is added to enhance flocculation. In the corrosion treatment system, phosphate is used as one of the corrosion inhibitors. Before reinjection, the blowdown will be treated with ferrous sulfate for phosphate removal. Polyelectrolyte will again be added to enhance flocculation.

The zeta potential study was established in order to study the surface reactions occurring in the silica removal system and to determine the optimum concentration of flocculant necessary for good silica and phosphate removal.

All particles in solution have a net surface charge (either positive or negative). Other ions in the solution tend to adsorb at the surface of these particles due to chemical, electrostatic, or physical adsorption. At the surface of the particle there is, therefore, one or more layers of charged ions. These layers become more diffuse as the distance from the particle increases. The zeta potential is the difference between the charge of the diffuse layer and the bulk solution.² In order to determine the zeta potential, a potential gradient is set up in a solution of charged particles and the rate of motion of the particles is measured. The zeta potential is proportional to the rate of motion and can be calculated by the Helmholtz Smoluchowski equation.³

The zeta potential or surface charge can be controlled through the addition of certain electrolytes or polyelectrolytes which adsorb onto the surface due to one of the following mechanisms: electrostatic adsorption,

physical adsorption, or chemical adsorption. Electrostatic adsorption results from the electrostatic attraction between the electrolyte and charged particle. These occur due to opposite charges. Simple electrostatic adsorption does not produce major changes in the zeta potential.⁴ Physical adsorption occurs due to van der Waal and/or Coulombic forces such as occur when like particles interact. In general, physical adsorption causes, as does electrostatic adsorption, little change in the zeta potential. Chemical adsorption, being a much stronger adsorption, causes the greatest zeta potential change. Chemical adsorption can be due to ion exchange type reactions or the formation of salt type minerals. In many cases physical or electrostatic adsorption can result in chemical adsorption.

Through a zeta potential study the mechanism of the surface reactions can be postulated and recommendations made concerning flocculation. One cannot state categorically that a colloid will be stable at a certain zeta potential, but the general rule for determining coagulation according to the zeta potential can be summarized according to Table 1 below.⁵

TABLE 1. STABILITY CHARACTERISTICS AS A FUNCTION OF ZETA POTENTIAL

<u>Stability Characteristics</u>	<u>Average ZP Millivolts</u>
Maximum agglomeration and precipitation	+3 to zero
Excellent agglomeration and precipitation	-1 to -4
Fair agglomeration and precipitation	-5 to -10
Threshold of agglomeration (agglomerates of 2 to 10 colloids)	-11 to -20
Plateau of slight stability (few agglomerates)	-21 to -30
Moderate stability (no agglomerates)	-31 to -40
Good stability	-41 to -50
Very good stability	-51 to -60
Excellent stability	-61 to -80
Maximum stability	-81 to -125

Figure 1 shows a theoretical curve in which zeta potential is plotted as a function of the pH of the system. In addition, the silica remaining in the system after flocculation and settling has occurred is plotted as a function of pH. Looking at only the zeta potential curve, the area where good flocculation should occur is determined by the pH's at which the zeta potential curve intersects the -10 mV and +10 mV lines. In this case, the area lies between pH 9.8 and 10.7. The silica versus pH curve shows that between pH 9.8 and pH 10.7 the silica has decreased to its low concentration and remains essentially constant.

In the following pages, experimental procedures and results of the zeta potential study are discussed as well as conclusions and recommendations resulting from the study.

2.0 PROCEDURE

Unless otherwise stated, the water used was Raft River geothermal at 60° C. The desired reagents were added. The solution was stirred at 120 RPM for 2 minutes and 20 RPM for 15 minutes. The zeta potential (particle motion) was measured using a Unitron Zeta Meter at 4X magnification using the optimum voltage designated by the conductivity of the solution. The conductivity was recorded for each test as was temperature and rate of motion. Tests were run to determine zeta potential of each step of the treatment processes for silica and phosphate removal.

The zeta potential was determined using the graphs provided with the zeta meter.⁵ The use of these graphs assume a viscosity and dielectric constant close to that for distilled water. Although this may or may not be true for the geothermal system, it is reasonable that there should be little or no change in these values among the solutions used in these zeta potential determinations. Since the work involves comparison of values, the graphs should be a good indication of what is happening.

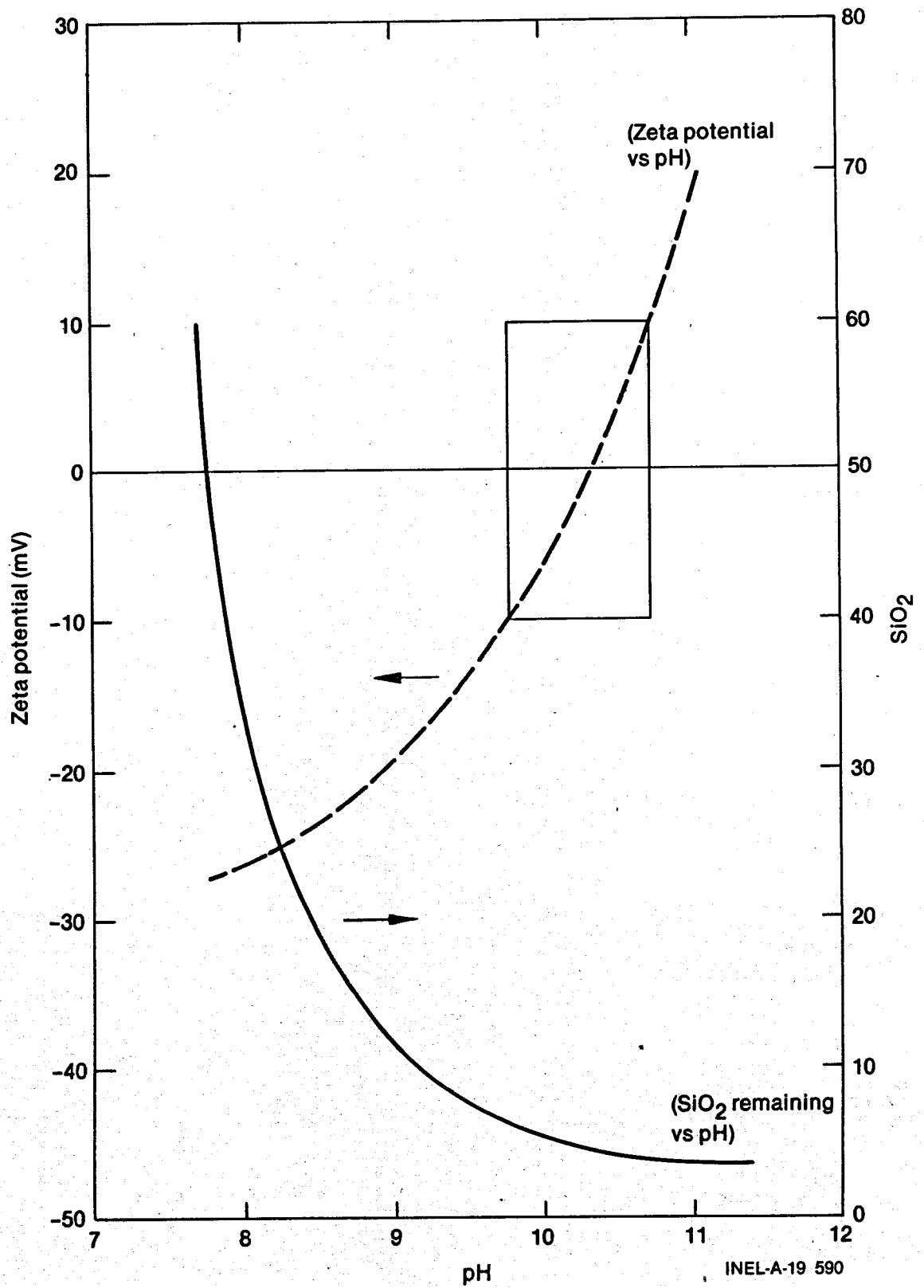


Figure 1. Theoretical Zeta Potential Curve

3.0 EXPERIMENTAL RESULTS

In order to check the zeta meter and the procedure for measuring the zeta potential, the zeta potential for Minusil was determined. Minusil is a natural silica produced by crushing sandstone. Minusil maintains a constant zeta potential of -55 ± 2 mV when suspended at 100 ppm in 100 ppm NaCl. With this suspension, a zeta potential of -56 mV was obtained.

The series of zeta potential studies performed on the geothermal fluid can be grouped into seven groups:

1. Zeta potential as a function of lime addition versus caustic addition.
2. Zeta potential as a function of calcium (CaCl_2) addition versus magnesium (MgCl_2) addition with no pH adjustment.
3. Zeta potential with 300 ppm MgO (MgCl_2) as a function of lime addition versus caustic addition.
4. Zeta potential with 300 ppm MgO (MgCl_2) present with and without pH adjustment as a function of calcium (CaCl_2) addition.
5. Zeta potential as a function of MgO (MgCl_2) concentration with pH adjustment.
6. Zeta potential as a function of Betz 1125L concentration.
7. Zeta potential study of the phosphate removal system.

3.1 Lime Addition Versus Caustic Addition

There is a positive increase (20 mV) in the zeta potential (Figure 2) initially with the addition of caustic. After this increase, there is little change in the zeta potential. The small change is probably due to electrostatic adsorption of sodium onto the negative silica. Adsorption is minimal, however.

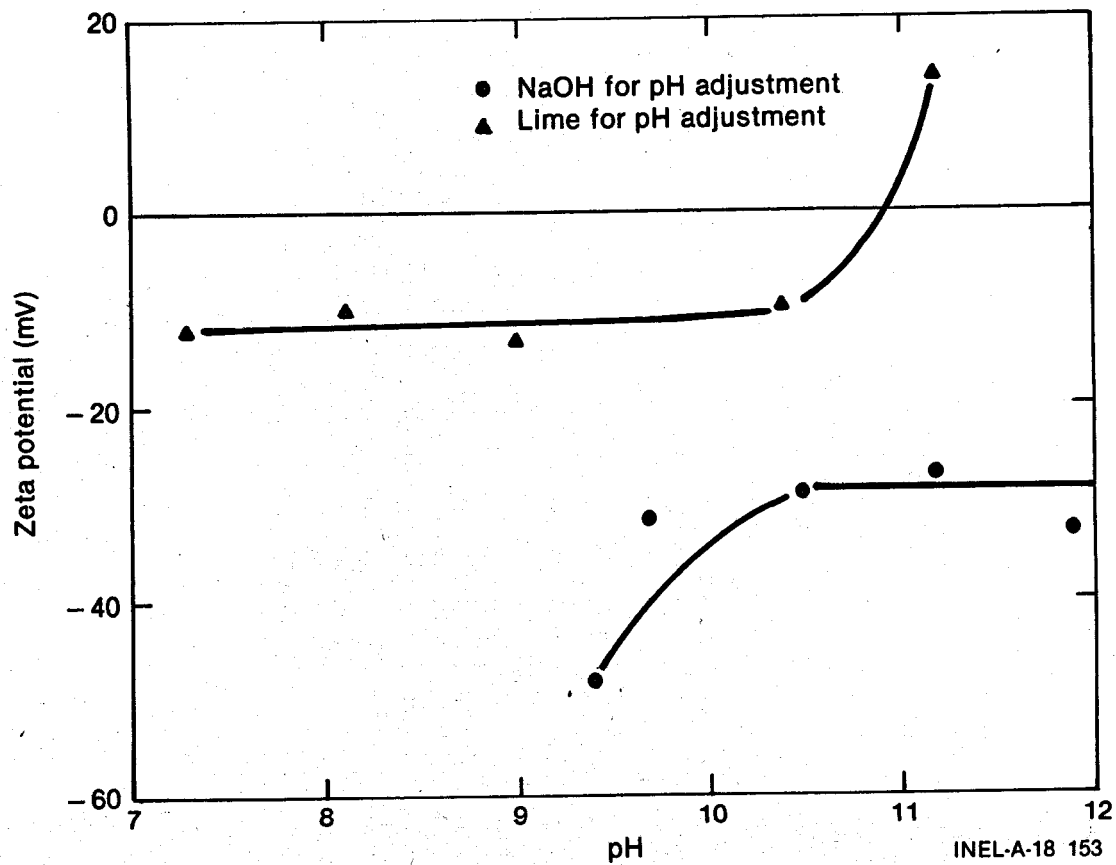


Figure 2. Zeta Potential Versus pH with Lime or Caustic Addition

With lime addition the zeta potential was linear and negative until a pH of 10.4. At this time, the zeta potential increases from -10 millivolts to +14 millivolts between pH 10.4 and 11.2. This large increase in charge with the curve passing through the point of zero charge (ZPC - point at which the surface is electrically neutral) shows at least electrostatic adsorption of the positive calcium and probably is an indication of the chemisorption of the calcium.

3.2 Calcium Addition Versus Magnesium Addition (no pH adjustment)

With both magnesium (as magnesium chloride) and calcium (as calcium chloride) addition to the geothermal water without pH adjustment, there is no major change in the zeta potential (Figure 3). With magnesium, the zeta potential passes through a minimum before approaching -20 mV again. With calcium addition, the zeta potential approaches -20 mV. Both curves show a lot of scatter in the data.

3.3 Lime Addition Versus Caustic Addition with 300 ppm MgO (as MgCl₂ Present)

Three hundred ppm of MgO (MgCl₂) was added to the geothermal fluid, and the system was treated with lime for pH adjustment. Initially there was little change in the zeta potential, then a linear increase from -10 to +44 mV (Figure 4). Chemical adsorption is occurring. Silica concentration decreases linearly from 150 to 4 ppm SiO₂. The reduction to 4 ppm occurs where the zeta potential is approaching zero. There is no increase in the silica concentration, however, as the zeta potential approaches +40 mV probably due to the nature of the electrolyte (MgCl₂) added to the system.

With caustic for pH adjustment (Figure 5) there is a linear decrease in the zeta potential from -20 to -60 mV between pH 8.5 and 10.5 due to the adsorption of the hydroxide onto the silica magnesium particle. The silica concentration was not determined due to the lack of sufficient coagulation.

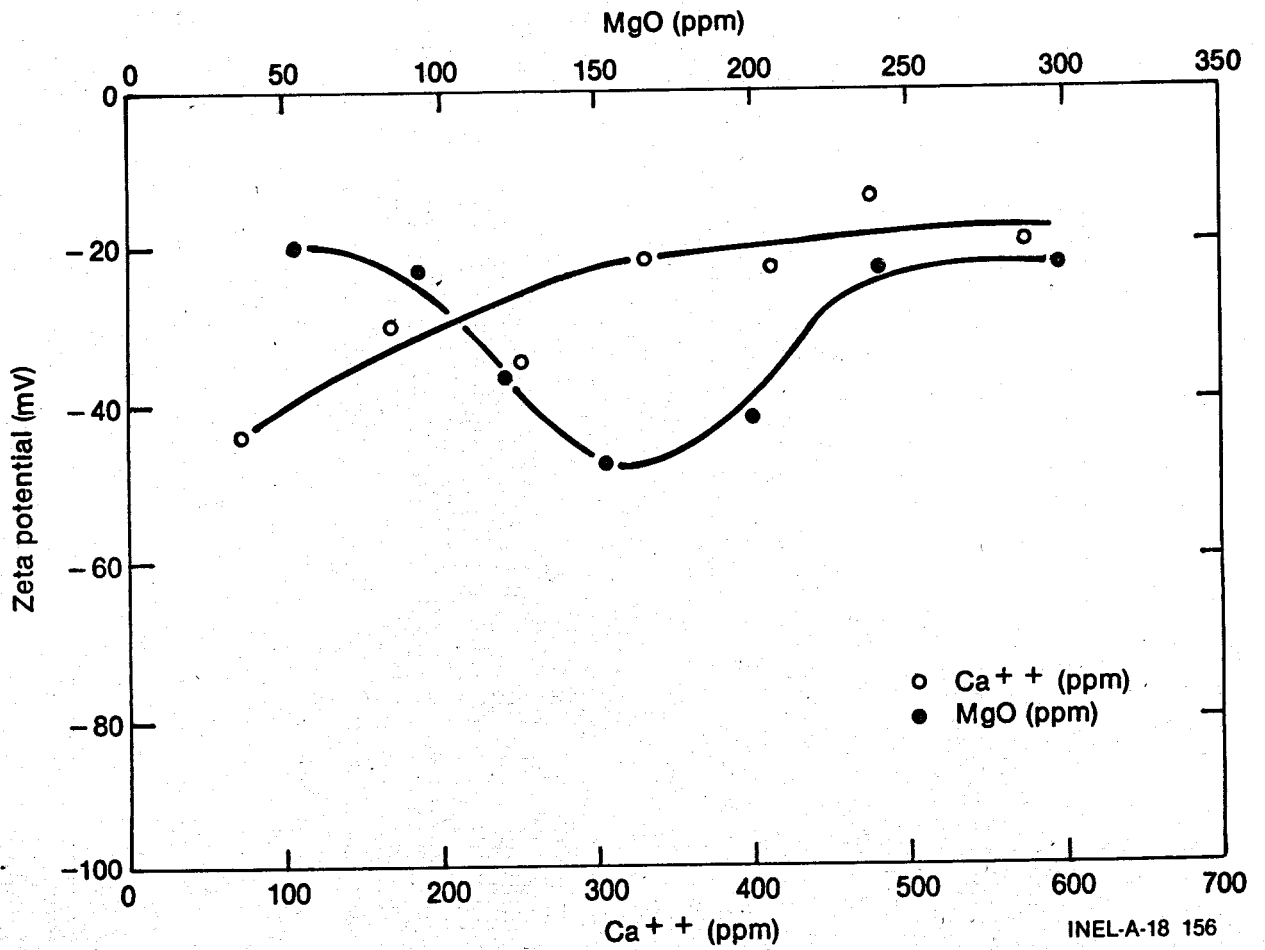


Figure 3. Zeta Potential Versus Calcium or Magnesium Concentration with No pH Adjustment

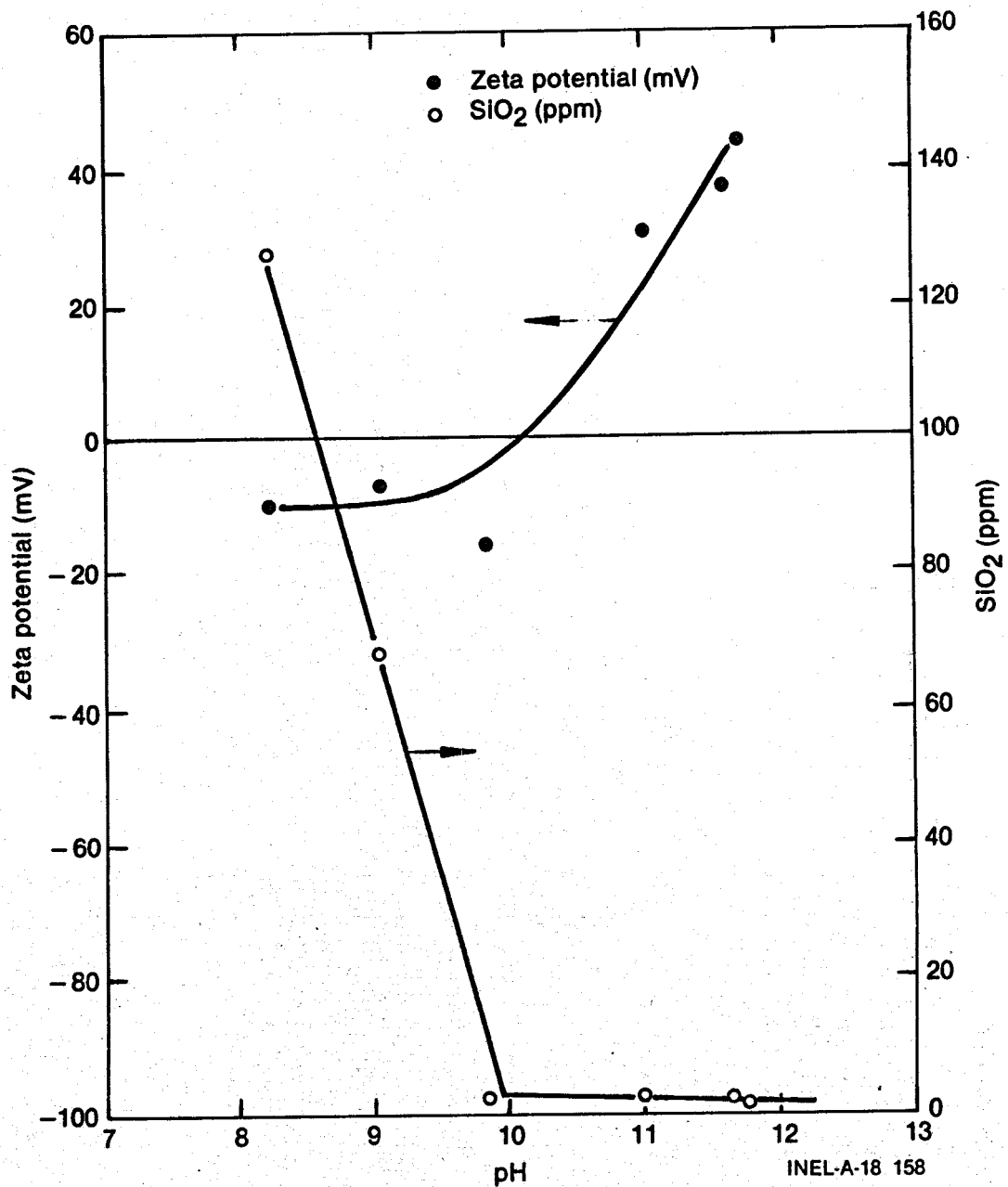


Figure 4. Zeta Potential Versus pH With Caustic Addition with 300 ppm MgO Present

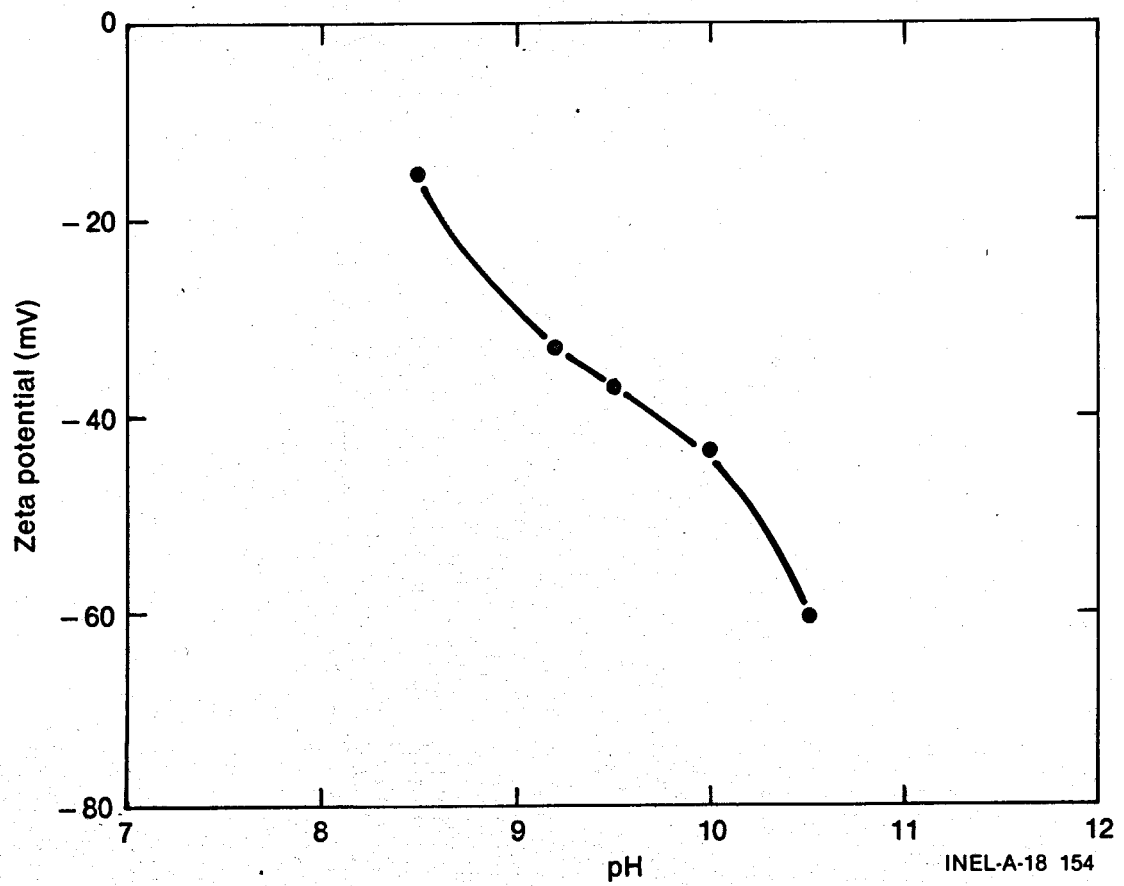


Figure 5. Zeta Potential Versus pH With Caustic Addition with 300 ppm MgO Present

3.4 Magnesium Oxide Concentration with pH Adjusted

The zeta potential increased exponentially with MgO addition when the pH was adjusted to 10.2 with lime (Figure 6) passing through the ZPC at 210 ppm MgO. The silica levels out between 180 and 250 ppm MgO. The increase from -28 to +11 mV and the change in sign indicates chemical adsorption is occurring.

3.5 Calcium Addition in the Presence of MgO (with and without pH adjustment)

Without pH adjustment (Figure 7) the zeta potential curve as a function of calcium (CaCl_2) concentration with 300 ppm MgO present looks similar to the one for calcium without MgO present. Some adsorption (electrostatic) is taking place but little change is occurring in the surface properties of the silica. The silica concentration was not decreased to any significant extent. When the pH is adjusted to 10.2 with caustic, there is a large change in the zeta potential from -73 millivolts to +39 millivolts with the addition of 200 ppm Ca^{++} as calcium chloride. The silica decreases to 2.4 ppm SiO_2 (Figure 7).

As a further check of the mechanism of adsorption the zeta potential was measured for magnesium oxide, added as magnesium chloride to deionized water, as a function of pH. The pH was adjusted with lime. The zeta potential shows a general trend to become more negative. Because lack of sufficient coagulation made the zeta potential measurement difficult, too few points were obtained for a zeta potential-pH curve.

3.6 Polyelectrolyte Addition

In order to determine the optimum polyelectrolyte necessary to coagulate the silica, the zeta potential was determined as a function of polyelectrolyte (Betz 1125L) concentration. Geothermal water was flash mixed with 300 ppm MgO (added as MgCl_2) and lime to pH 10.3. The polyelectrolyte was added as a 0.2 w/o solution to the slurry and stirred 15 minutes. The zeta potential decreases exponentially from +33 millivolts to -70 millivolts at 20 ppm due to the adsorption of the anionic polyelectrolyte (Figure 8). The silica remains at its lowest level between

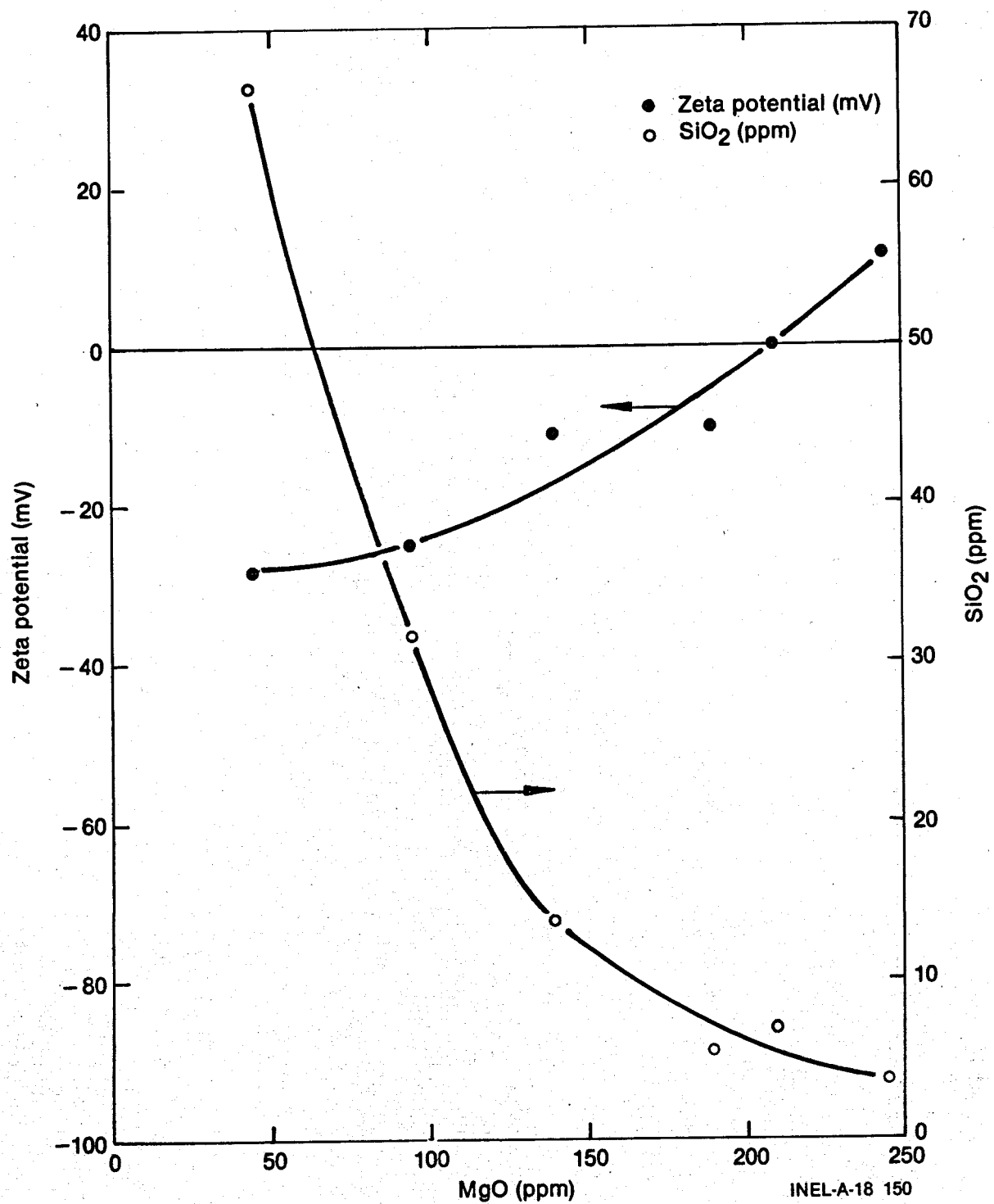


Figure 6. Zeta Potential and Silica Concentration Versus Magnesium Oxide Concentration with pH Adjusted to 10.2 with Lime

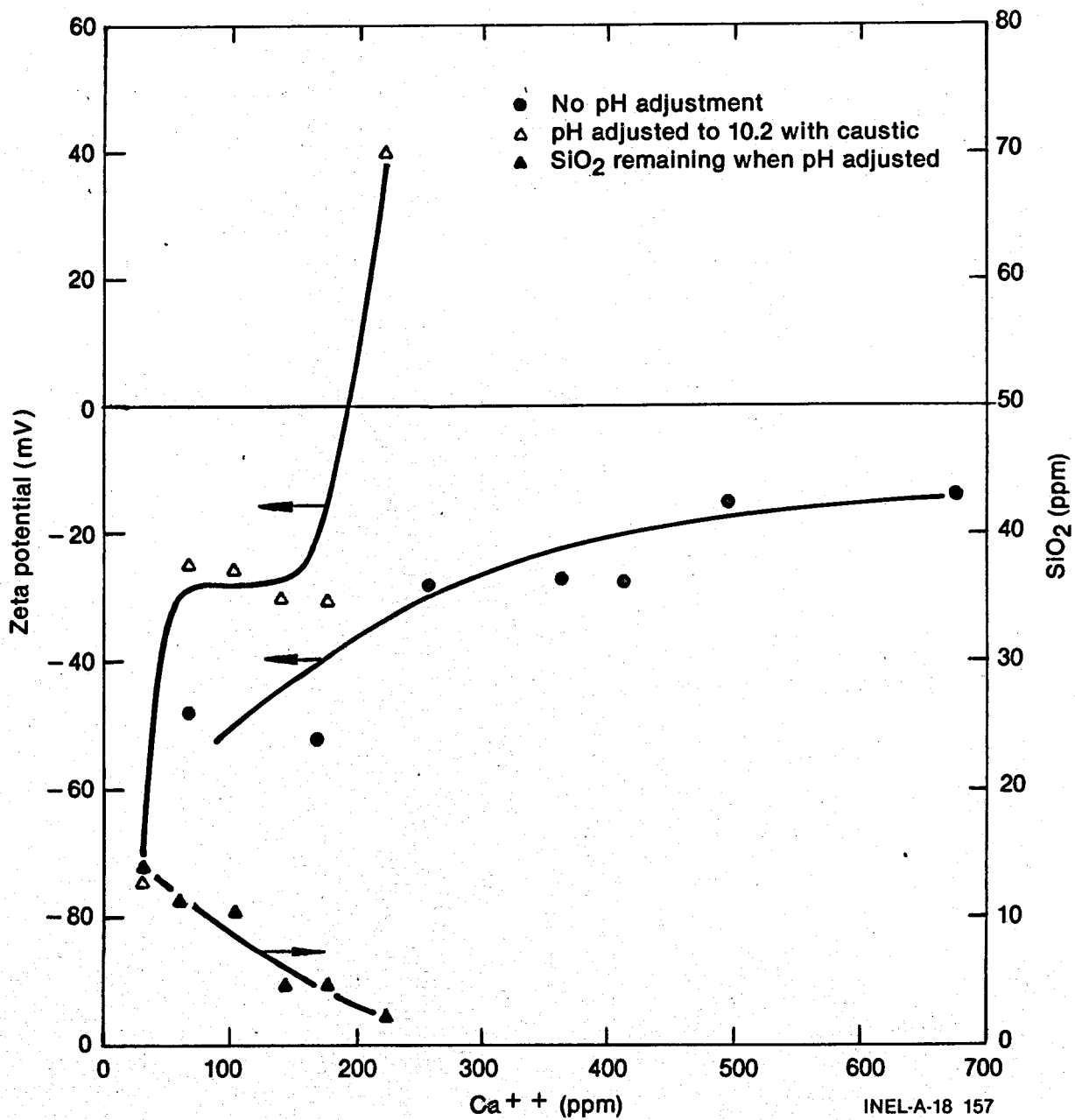


Figure 7. Zeta Potential and Silica Concentration as a Function of Calcium (as CaCl₂) Addition in the Presence of 300 ppm MgO

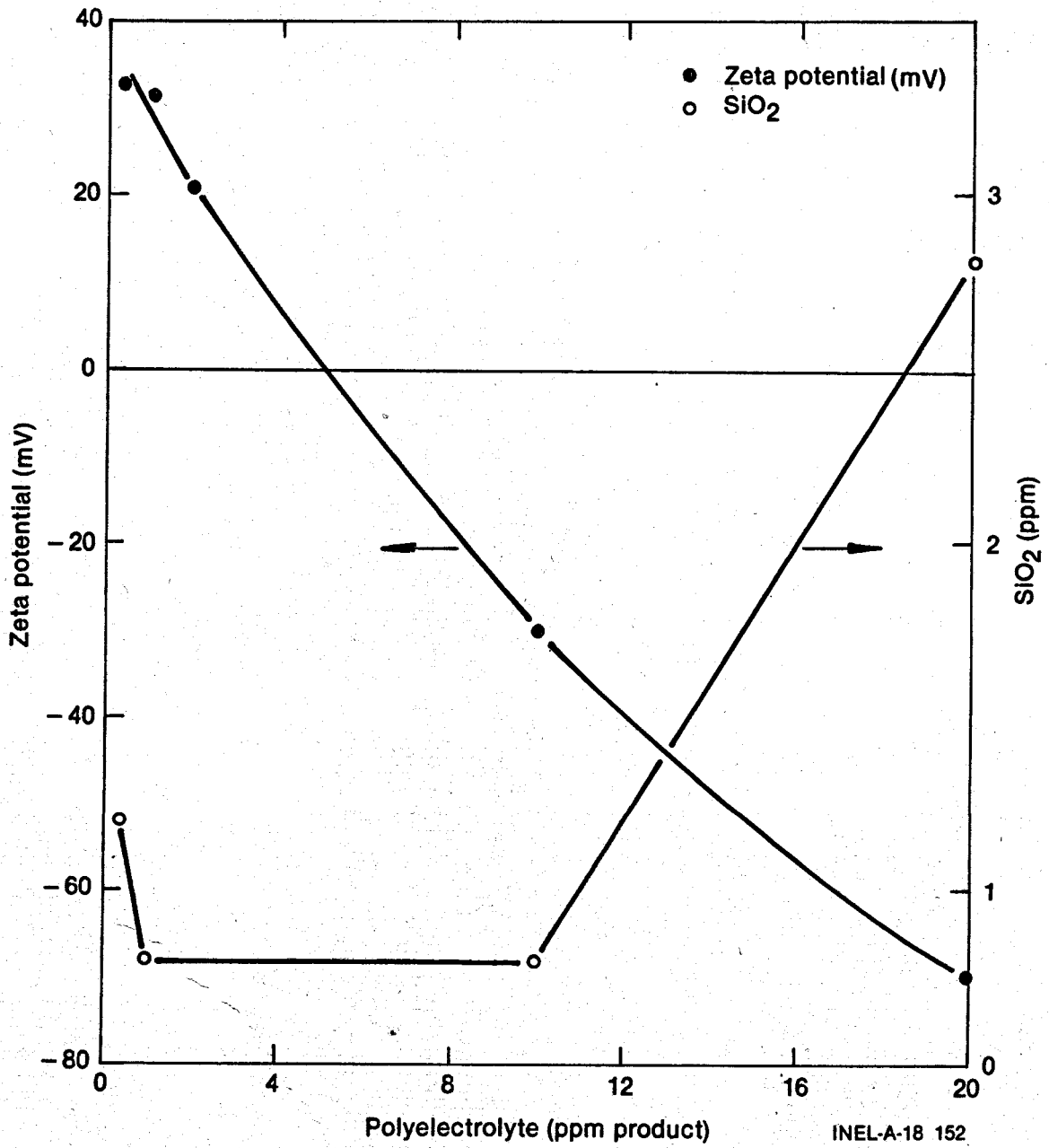


Figure 8. Zeta Potential and Silica Concentration as a Function of Betz 1125L Concentration

one and eight ppm. With additional polyelectrolyte, the silica increases again. This agrees with Slater, et al.,⁶ "In large doses the polyelectrolytes act as protective colloids . . . Their action as flocculants is confined to very low concentrations." Even with 0.2 ppm of polyelectrolyte, the silica concentration, 1.2 ppm SiO₂, is lower than without electrolyte addition. Duplication of the work showed that at 8 ppm of polyelectrolyte, there was a tendency toward much higher silica levels and variations in the zeta potential.

3.7 Phosphate Removal From the Tower Blowdown

In the zeta potential study of the phosphate removal system, 500 ml of tower blowdown was adjusted to 40 ppm total phosphate with Betz 35-A (a Betz product having 35 w/o total phosphate). Ferrous sulfate was added to the system, and the pH was adjusted to 10.2. The zeta potential was determined as a function of the iron concentration. With this system, there was little change in the zeta potential; however, the zeta potential did go to zero between 30 and 38 ppm of Fe⁺⁺ and remained there (Figure 9). Total phosphate tended to level off between 20 and 30 ppm Fe, indicating this is the optimum iron concentration for phosphate removal. However, at this concentration the particle is negative.

Betz 1125L, an anionic polyelectrolyte, was recommended as a flocculation aid for the phosphate reduction system of the 5MW(e) Geothermal Pilot Power Plant. For successful use of an anionic flocculant, the particle must be positive. In order to determine the pH at which the iron-phosphate particle becomes positive, 40 ppm of phosphate (Betz 35-A) and 30 ppm iron (ferrous sulfate) was added to domestic water. The pH was adjusted with lime. Figure 10 shows that the zeta potential does not pass through zero until pH 11.5. An additional test was conducted to determine the efficiency of Betz 1125L at pH 11.0 and 11.7, using the above concentrations of iron and phosphate. The zeta potential was determined as a function of the concentration of polymer added (Figure 11). Much better phosphate reduction was obtained at pH 11.7, where the particle was positive. The optimum reduction occurred at 1 to 2 ppm of the polymer. Such a high pH, however, is costly.

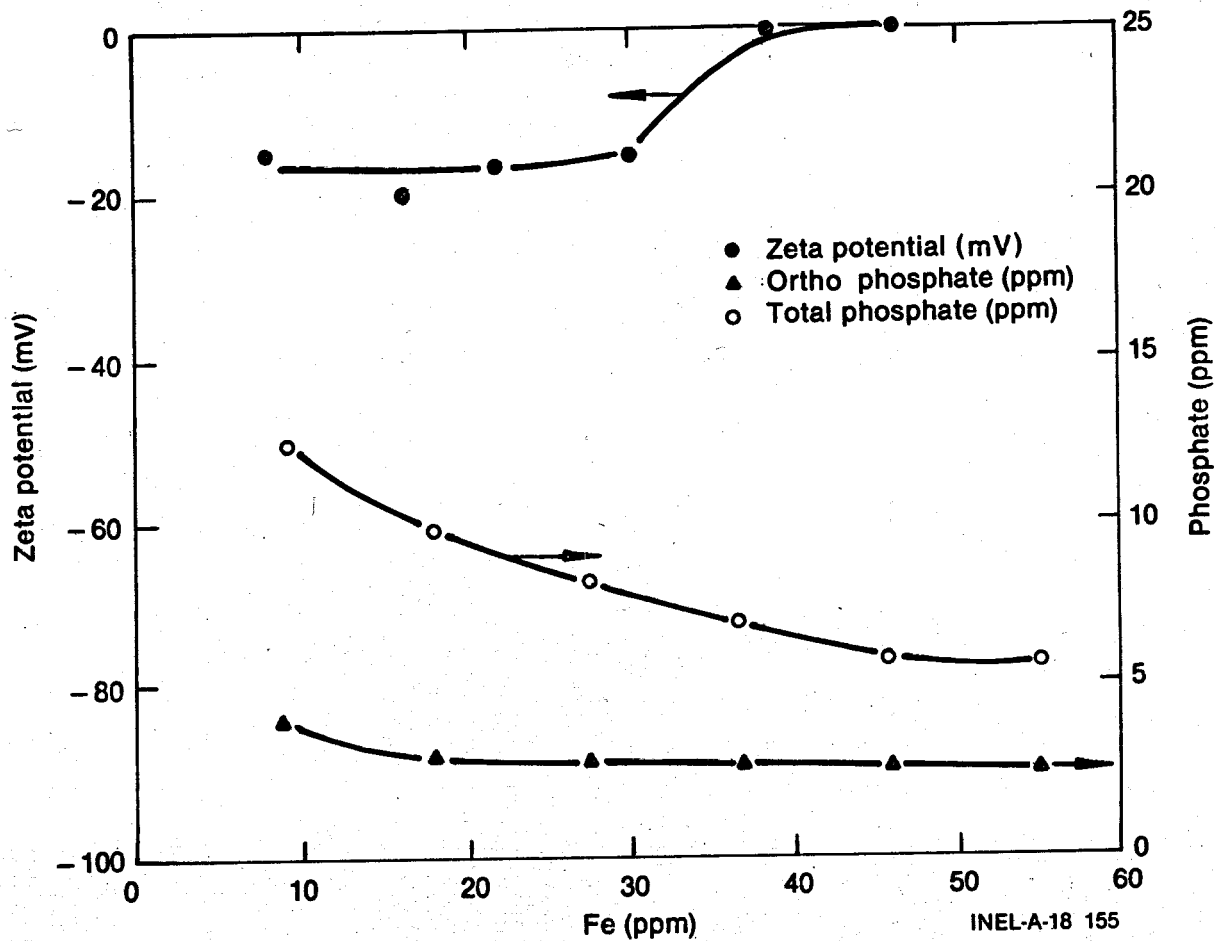


Figure 9. Zeta Potential and Phosphate Concentration of the Tower Blowdown as a Function of Iron Concentration

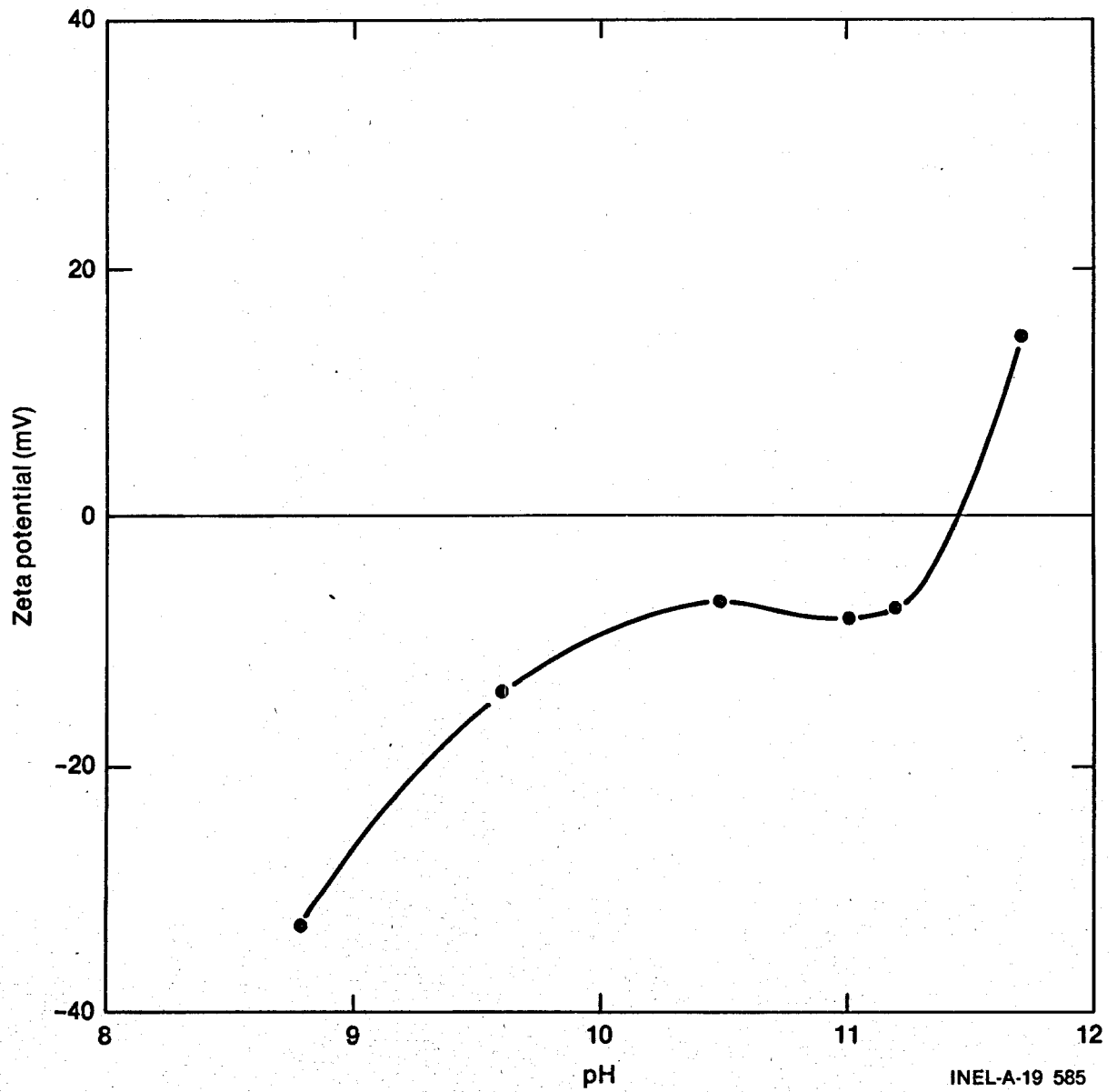


Figure 10. Zeta Potential of the Iron-Phosphate System as a Function of pH

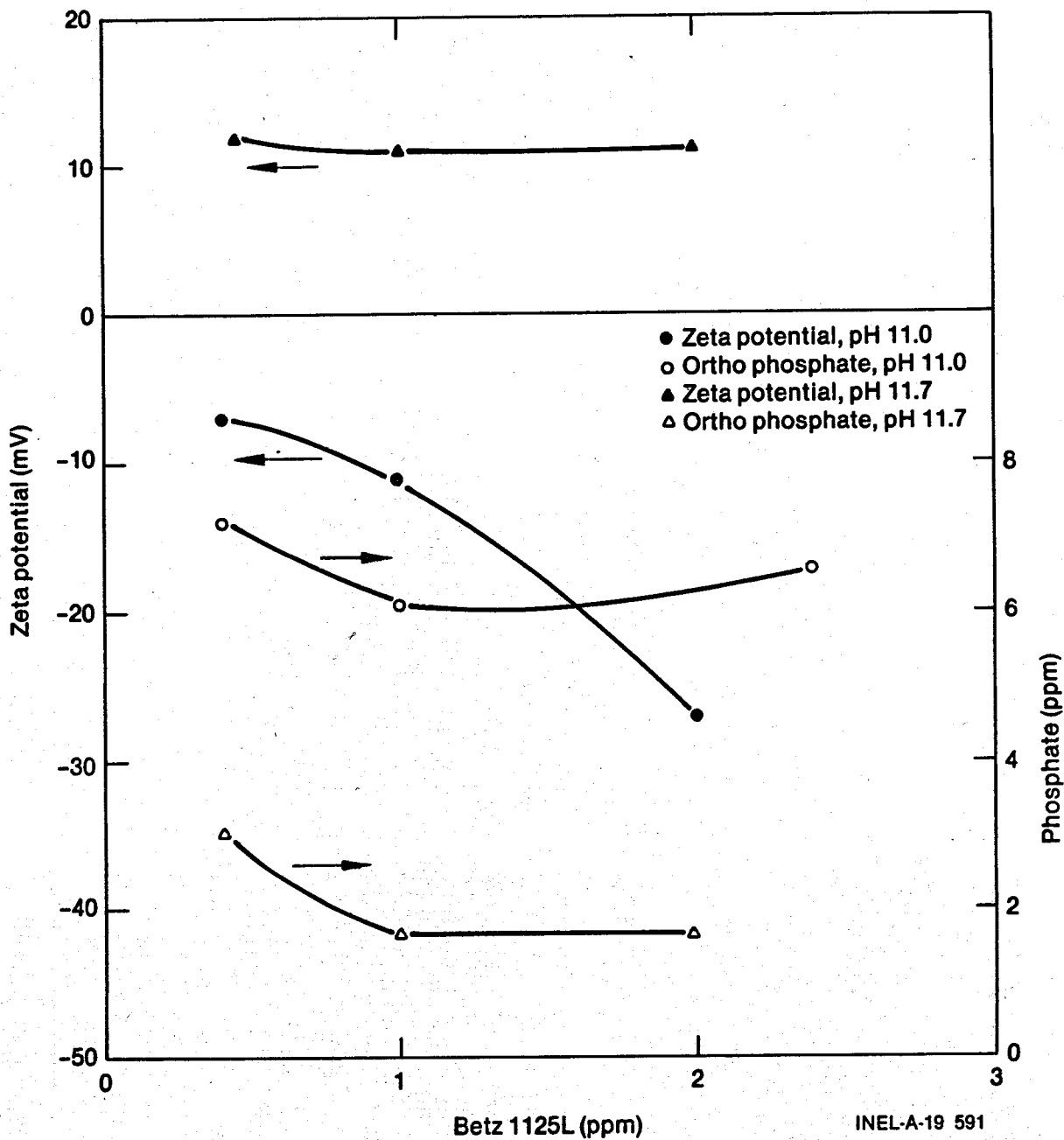


Figure 11. Zeta Potential and Phosphate Concentration of the Iron-Phosphate System as a Function of pH and Betz 1125L Concentration

The zeta potential of the iron-phosphate system was examined at pH 9, using several Betz cationic polymers as a function of polymer concentration. The results are shown in Figure 12. The zeta potential curve for 1175 and 1185 remains negative from 0.2 to 10 ppm of the polymers. The floc was extremely fine and slow settling. Use of three of the polymers caused the system to become positive. However, the zeta potential curves for the 1180 and 1190 show very little range at which good flocculation should occur. Betz 1195 shows a more stable curve passing through zero to +6 mV then remaining zero along the remainder of the concentration range to 10 ppm. In all cases, the 1195 resulted in the formation of large flocs and good settling.

A zeta potential curve as a function of pH using 2 ppm of Betz 1195 and lime for pH adjustment in the iron-phosphate system (Figure 13) indicates the zeta potential passes through zero near a pH of 9.1 or 9.2. Using pH 9.2, the zeta potential of the iron phosphate system was determined as a function of 1195 concentration. Figure 14 shows the zeta potential passes through zero at about 3.0 ppm 1195 and reaches +10 mV at 4 ppm 1195, indicating the optimum concentration would be 2 to 4 ppm Betz 1195. Both total and ortho phosphate increases with the use of 6 ppm of Betz 1195 (Figure 15).

4.0 DISCUSSION AND CONCLUSIONS

The zeta potential data suggests the following adsorption process occurs in silica removal. Through the addition of magnesium chloride and pH adjustment with either lime or caustic, magnesium hydroxide is formed. There is adsorption between the magnesium hydroxide and the silica. With the addition of calcium ion as either lime or calcium chloride, there is a bridging type adsorption between the calcium and the silica magnesium hydroxide particles.

The adsorption process is favored by the following observations:

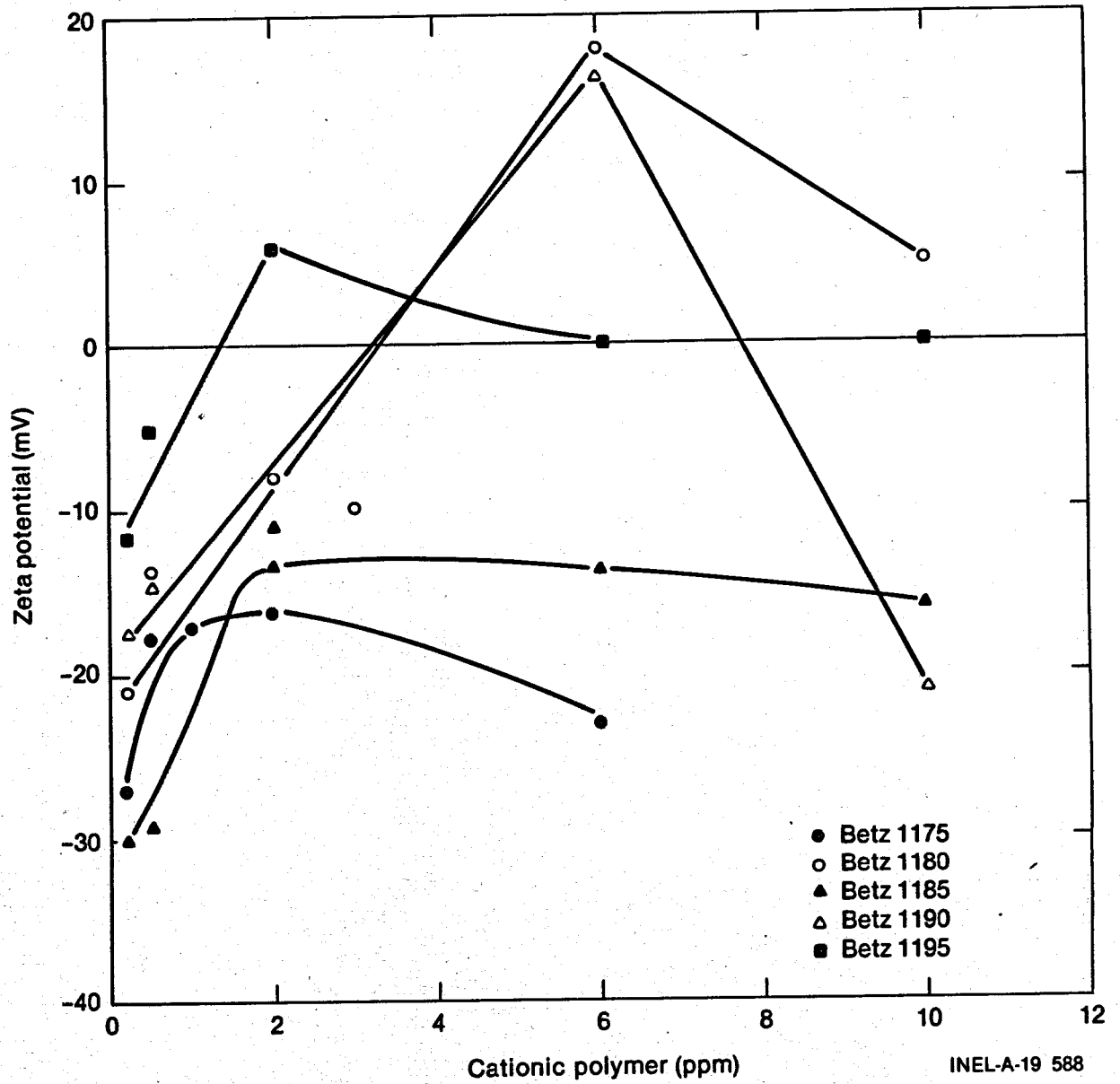


Figure 12. Zeta Potential of the Iron-Phosphate System as a Function of Cationic Polymer

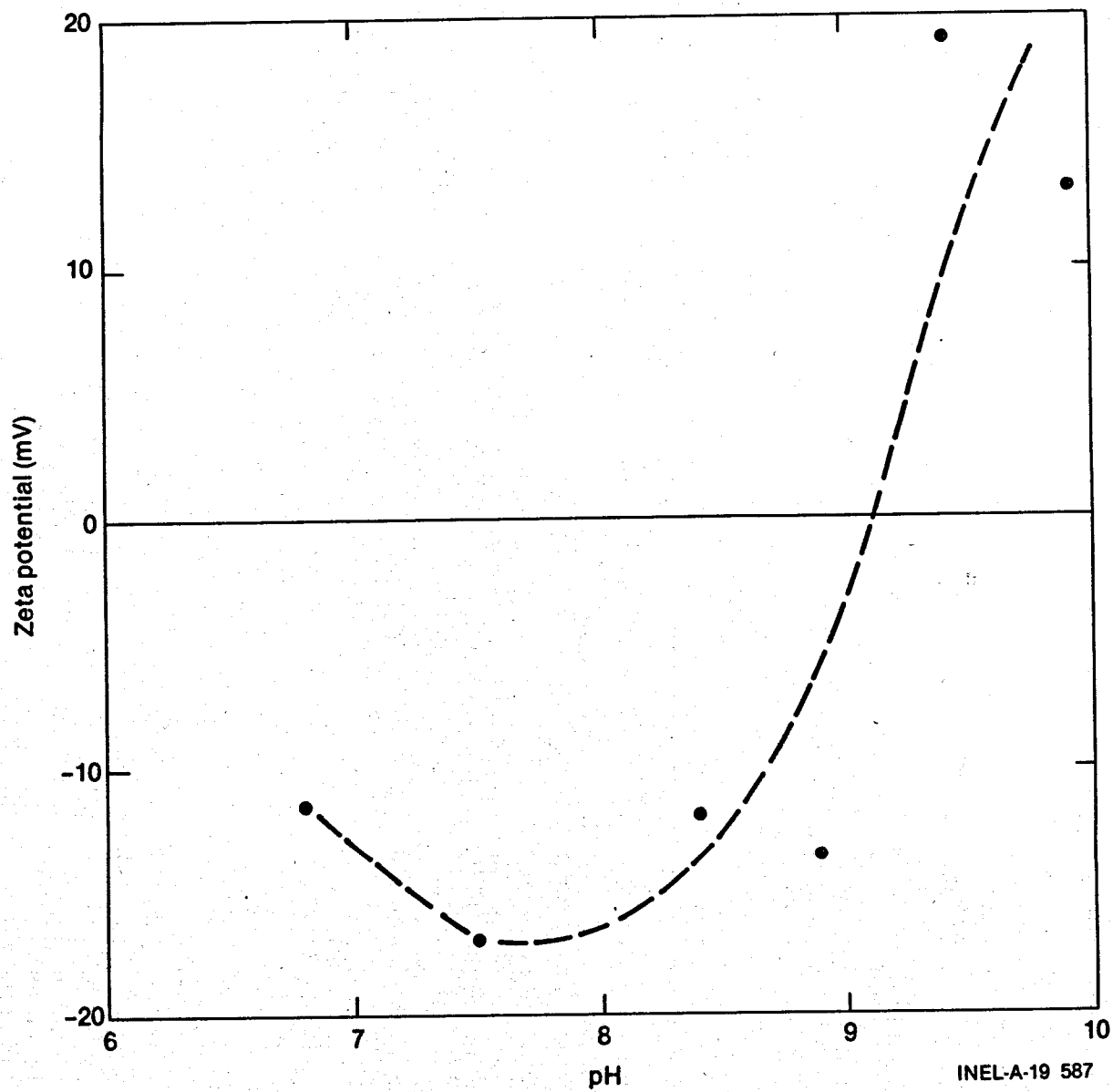


Figure 13. Zeta Potential of the Iron-Phosphate System with 2 ppm Betz 1195 as a Function of pH

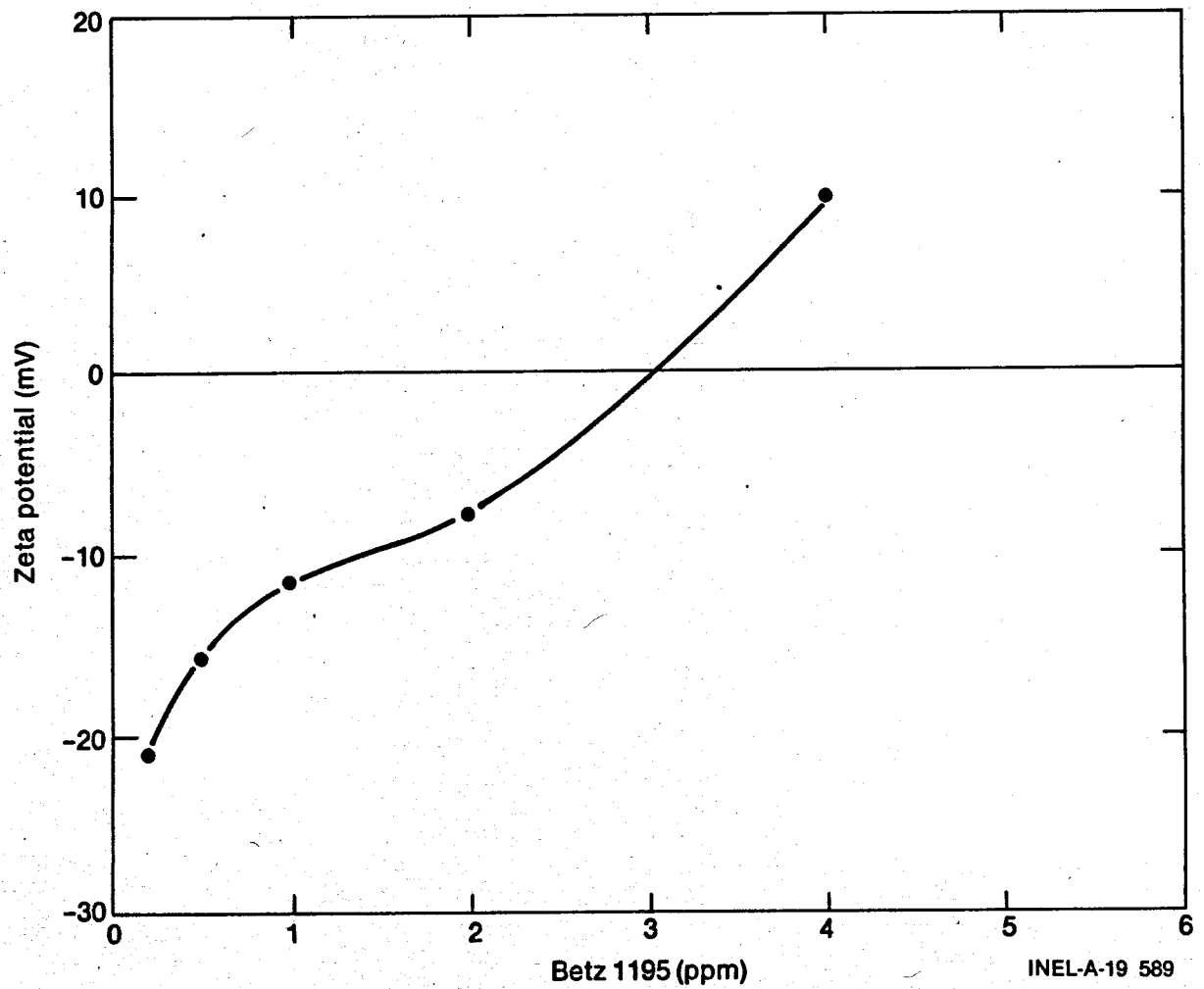


Figure 14. Zeta Potential of the Iron-Phosphate System at pH 9.2 as a Function of Betz 1195 Concentration

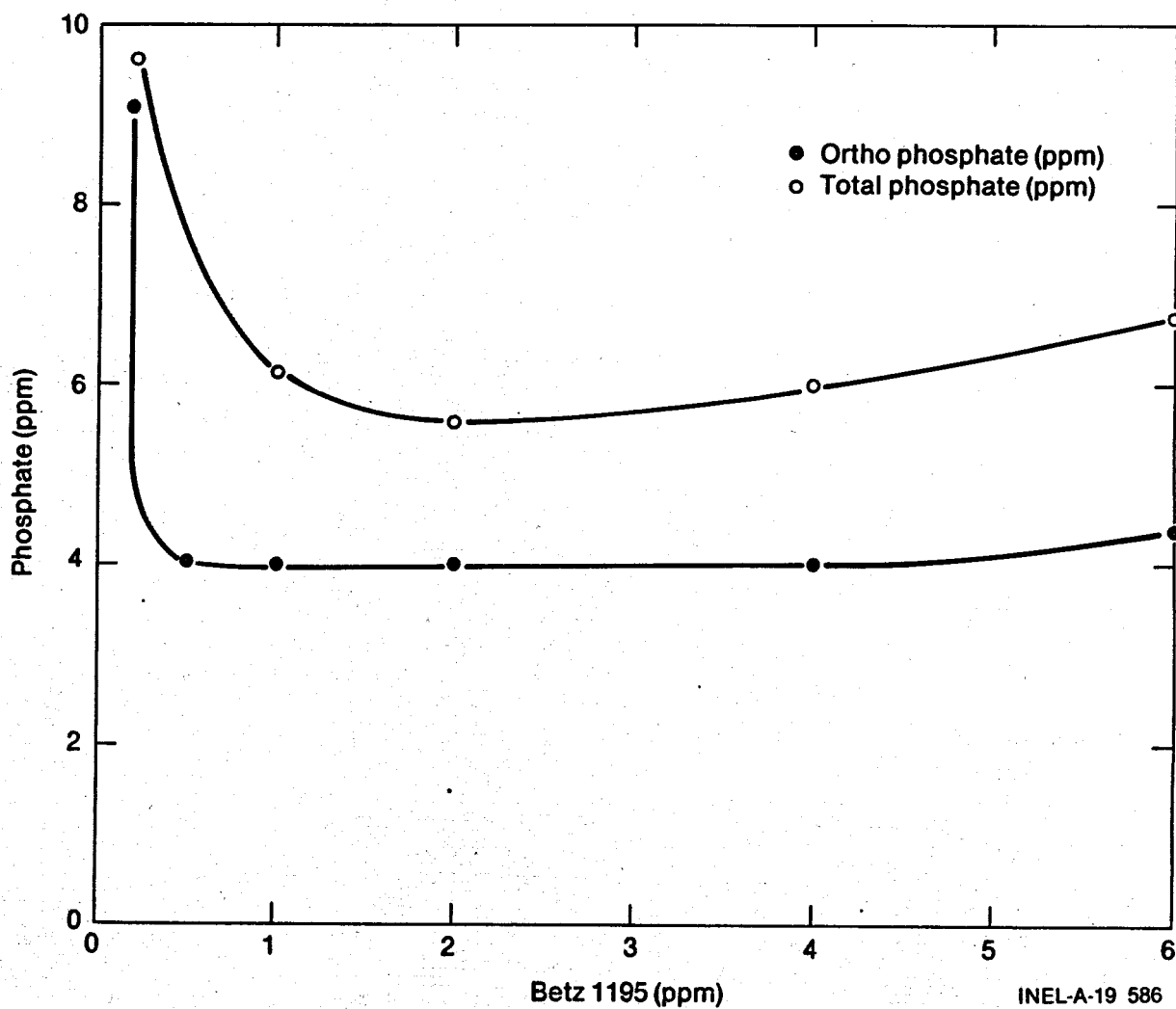


Figure 15. Total and Ortho-Phosphate Remaining in the Solution at pH 9.2 as a Function of Betz 1195 Concentration

1. The addition of magnesium or calcium ion without pH adjustment causes a small positive increase in the zeta potential indicating a weak adsorption.
2. The addition of lime without magnesium present causes a large positive increase in the zeta potential. This is due to the adsorption of the calcium onto the negative silica - the formation of a salt; however, with this adsorption, there is little coagulation or settling of the silica.
3. When 300 ppm of magnesium oxide is added to the geothermal water prior to pH adjustment with lime, the zeta potential becomes positive. In addition, there is a linear decrease in the silica concentration.
4. When 300 ppm of magnesium oxide is added to the geothermal prior to pH adjustment with caustic, the zeta potential becomes increasingly more negative. This is probably due to the adsorption of the hydroxide onto the silica magnesium particle. If the sodium is adsorbed, the adsorption causes little change in the zeta potential.
5. With 300 ppm magnesium oxide present, the addition of calcium chloride causes little change in the zeta potential with no pH adjustment.
6. With 300 ppm magnesium oxide present, and the pH adjusted to 10.2 with caustic, the zeta potential becomes increasingly more positive with calcium addition.
7. When 300 ppm of magnesium oxide is added to deionized water, the zeta potential shows a general tendency to become more negative as a function of pH when lime is used for pH adjustment.

Polyelectrolyte adsorption appears to be due to the chemical adsorption of the anionic polyelectrolyte onto the now positive silica complex. Optimum silica reduction is obtained between one and eight ppm of Betz 1125L; however,

other data indicate a significant amount of scatter in silica concentration and zeta potential at eight ppm of the polyelectrolyte. At 0.2 ppm of polyelectrolyte, there is still a reduction in silica.

The zeta potential study of the phosphate reduction system, using ferrous sulfate, indicated the optimum reduction occurred at approximately 30 ppm of iron. Using 30 ppm of iron and lime for pH adjustment, the iron-phosphate particle becomes positive after pH 11.5. Betz 1125L is much more effective at pH 11.7 than 11.0 with the optimum reduction occurring at 1 to 2 ppm of 1125L. Use of a cationic polymer results in operation at a much lower pH. Of the 5 cationic polymers used, Betz 1195 showed a more stable pH curve with the optimum pH being 9.2 adjusted with lime and the optimum polymer concentration being 2 to 4 ppm of Betz 1195.

5.0 RECOMMENDATIONS

The zeta potential data and silica concentrations indicate an optimum MgO concentration, added as $MgCl_2$, is between 150 and 250 ppm of MgO. This is substantially lower than the recommended 450 ppm of MgO. This recommendation was based on previous work (Suciu and Wikoff), in which conditions were more harsh. The cost reduction, such a reduction in MgO concentration would result in, as outlined below:

TABLE 2. COMPARISON OF COST WITH REQUIRED MgO CONCENTRATION

<u>MgO (ppm)</u>	<u>\$/year</u>
150	57,000
250	94,000
450	138,000

The optimum polyelectrolyte concentration, as indicated by the data, lies between one and eight ppm of Betz 1125L. The lower concentration is recommended due to the increased silica concentration sometimes obtained at the upper range while obtaining the data. Depending on the end silica concentration desired, the

data indicates that even with 0.2 ppm of the polyelectrolyte silica is less than two ppm. Betz Corporation recommended a concentration of four ppm. The data here indicates that a concentration of one ppm will result in the same reduction. The cost reduction is outlined below:

TABLE 3. COMPARISON OF COST WITH REQUIRED POLYELECTROLYTE CONCENTRATION

<u>Polyelectrolyte (ppm)</u>	<u>\$/year</u>
0.2	260
1.0	1,220
2.0	2,450
4.0	4,980

The zeta potential study for the iron-phosphate system indicates the optimum iron concentration lies between 20 and 30 ppm iron. The optimum pH using the cationic polymer, Betz 1195, is 9.2 with the pH being adjusted with lime. Optimum polymer concentration is 2 to 4 ppm of Betz 1195. Further optimization will result from the operation of the phosphate reduction system since the zeta potential study has only looked at the iron-phosphate particle in domestic water. Dispersants as well as zinc sulfate will be present in the blowdown water. The zeta potential will be examined again when the blowdown system is operating.

Although the zeta potential study gives some starting concentration for the magnesium oxide, Betz 1125L, iron, and Betz 1195, further optimization should result from the operation of the plant since other elements may play a role there in determining the surface chemistry, and consequently, the necessary concentrations.

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