EVALUATION OF ACIDS AS A FILTER AID
IN MICA PROCESSING
BY ZETA POTENTIAL MEASUREMENTS

by
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ABSTRACT

Zeta potential measurements have been performed on products from Diamond Mica. There should be good correlation between high negative zeta potentials and good dispersion, and low negative zeta potentials and good filtration. Addition of sodium tetra phosphate increases the negative zeta potentials, and addition of acid decreases them.

HNO_3 and HCl were found to be the most efficient acids on a normality basis, and the action of these acids could partly be reversed by filtration and drying. Other acids like divalent H_2SO_4 and divalent acids might adsorb stronger on the mica so that the effect could not easily be reversed.

INTRODUCTION

Diamond Mica Company operates a wet grinding plant for mica. The flowsheet is shown in Figure 1.

The feed is ground in a number of mullers at a moisture content of 12%. Sodium pyrophosphate, 1 lb/ton, is added here as a dispersant. The mica pulp is diluted to 12% solids after grinding; and the coarser particles are settled out in traps before the ground mica goes to settling tanks, where the mica is settled out for 6 hours. Overflow from the settling tanks will contain clay, which is discarded after a subsequent resettling. The main purpose of the pyrophosphate is to disperse the clay so it can be removed by decanting.

The dispersive effect of the sodium pyrophosphate makes the ground mica extremely hard to filter. One lb/ton of hydrochloric acid is therefore added before filtration in a pressure filter. Filtration is followed by drying and dry screening.

Addition of sodium pyrophosphate will increase the pH of the pulp and increase the negative value of the zeta potential of the mica particles. The negative value of the zeta potential will be increased by adsorbtion of negatively charged OH^- ions and possibly $P_2O_7^{4-}$ ions. HCl has to be added to break this dispersion. The pH is lowered below 7 where the OH ions do not dominate, and the negative value of the zeta potential will decrease.

HCl is unwanted in the process because it attacks the liner of the dryer. H_2SO_4 has been tried as a substitute, and it helps the filtering all right. The final product must, however, easily be dispersed; and this was difficult when H_2SO_4 was used. Two things may account for the difference:

1) Cl^- is an univalent ion and not strongly adsorbed on the mica. It will therefore be better removed during filtering together with the water phase than the H_2SO_4.

2) HCl is volatile, and the remaining acid may be driven off during the drying operation.

PURPOSE OF TESTWORK

The purpose of the project was to investigate whether or not zeta potential measurements could help us to gain insight into the dispersion and floculation of the ground mica and, if possible, to find an alternate to HCl.

SAMPLES AND PROCEDURES

The samples for the test work were taken November 29, 1979. The samples were numbered 4545.
1) Muller discharge. No pyrophosphate added this time.
2) Settling tank underflow, normal reagents added.
3) Filter feed, normal reagents added.
4) Filter cake, normal reagents added.
5) Final product, normal reagents added.
6) Settling tank overflow, normal reagents added.
Another sample 3, filter feed, was taken February 28, 1979.

The samples could be treated different ways. The zeta measurement could not be done directly on the sample as it was because individual particles had to be followed in a microscope. Dilution to increase visibility would change the chemical composition of the sample. Instead the pH of the sample was measured first, then it was centrifuged to remove practically all solid particles from the water phase. Some drops of the original slurry had to be added to the filtrate in order to re-introduce any particles to trace.

The pH measurement was difficult. It took some time before a stable value value was reacted. The pH was, as a rule, measured both on the sample and on the filtrate; and the difference between those two measurements was in the range 0 - 0.5 pH units. Another measurement on the sample was conductivity measured in micromho/cm. (1 mho = $\frac{1}{1\ ohm}$) Here the conductivity of the filtrate is usually measured. It will be higher than the conductivity of the slurry because part of the slurry volume will be occupied by an insulator. The apparent slurry conductivity will therefore be a function of both electrolyte concentration and pulp density.

Zeta potential measurements were carried out as described in an earlier report (79-3-P). Plant samples were centrifuged as received prior to the measurement. Muller discharge samples to be used for laboratory investigation were diluted to 10-15% solids with distilled water. The pulp was then agitated and allowed to settle half a foot

in an hour in a graduate cylinder. Supernatant liquid was then drawn off. The thickened pulp was in the 20-30% solids range. In contrast to plant practice, sodium pyrophosphate was not added before thickening. In the tests where it was needed, one-half the nominal amount was added afterwards. The other half was supposed to be lost with the slimes.

PLANT SAMPLE INVESTIGATIONS

Conductivity, pH, and zeta potential were measured on all plant samples. Some could be centrifuged as described, but the filter cake and dryer product had to be repulped with distilled water. This would effect the measurements to some extent and results with different dilution prior to centrifuging are shown in Table 1 for filter feed.

TABLE 1
FILTER FEED MEASUREMENTS
Different Dilutions with Distilled Water

Water Dilution	Conductivity Micromho	pH	ZP mV
1 = 1	650	6.4	-48
1 = 2.5	270	6.7	-52
1 = 5	135	6.7	-54
1 = 10	65	7.0	-54
1 = 20	37	7.1	-59
1 = 40	20	7.2	-52
1 = 80	13	7.1	-51

The other measurements performed on the samples taken in the plant are shown in Table 2.

TABLE 2
MEASUREMENTS ON SAMPLES DIRECTLY FROM PLANT

Sample	% Solids	ZP mV	pH	Conductivity Micromho
*1 Mill discharge	28	-52	7.0	150
2 Settler underflow	21	-65	8.3	260
6 Settler overflow	1	-54	7.7	180
3 Filter feed	31	-48	6.4	650
4 Filter cake repulped	20	-61	7.32	84
5 Dryer product repulped	20	-56	7.77	160
**3 Filter feed	44	-48	6.61	530

*This sample was without sodium pyrophosphate.
**This sample was taken separately February 28, 1979.

One should note the settler underflow and overflow samples. The purpose of the sodium pyrophosphate addition is to disperse the clay—give it high negative zeta potentials. Whether this has been successful or not is hard to tell from the data. The particles which have been tracked for zeta potential calculation have most likely been mica particles. The clay particles are probably smaller and harder to find and follow.

The same results are also plotted in Figure 2 together with lab data obtained from the Muller discharge sample. pH on those are modified with HCl and pyrophosphate. There is a distinct connection between pH and zeta potential. The spread of the curve points are caused by difficulties in pH measurements $\pm$ 0.3 pH units, zeta potential measurements $\pm$ 2-3 mV and different sample treatments.

The stability of the mica suspensions in water can be judged from Table 3 (after Riddick 2)

TABLE 3

Stability Characteristics	ZP in mV	
Strong agglomeration and precipitation	+5	-5
Threshold of agglomeration	-10	-15
Threshold of delicate dispersion	-16	-30
Moderate stability	-31	-40
Fairly good stability	-41	-60
Very good stability	-61	-80
Extremely good stability	-81	-100

The settler underflow is in the region of very good stability and therefore difficult to filter as it is, because the mica particles will repulse each other strongly and thus trap water between them.

Acid addition reduces the zeta potential to the region of fairly good stability where filtration apparently is possible. According to Figure 2, a stronger acid addition would have made filtration even easier, but plant practice indicates that this makes the subsequent redispersion difficult. Filtering and drying do increase the negative value of the zeta potential above the filter feed value, but not quite to the settler underflow value. The problems with reproductivity repulping those two products should be borne in mind here.

It can also be seen that acid addition gives a larger contribution to sample conductivity than did the sodium phosphate addition.

LABORATORY INVESTIGATIONS

Simulation of plant conditions was attempted in the Laboratory.
Sodium pyrophosphate was first added to the mica slurry, then acid.
The samples were then filtered and dried. Smaller samples were cut at
each stage for zeta potential measurement. The results are shown in
Table 4.

TABLE 4
PLANT OPERATION SIMULATED IN BATCH ZETA POTENTIALS
OF THE MICA AT VARIOUS STAGES OF OPERATION

Pyrophash lbs/ton	Acid Type lbs/ton		No Acid	After Acid	After Filter	After Dryer
0	HCl 37%	pH	7.1	4.3	5.1	5.5
		Cond	78	560	120	100
		ZP	-56	-3	-23	-30
0.5	HCl 37%	pH	7.4	4.6	5.4	5.7
		Cond	105	420	105	78
		ZP	-54	-10	-18	-33
0	H2SO4 100%	pH	7.1	4.0	4.4	5.0
		Cond	78	580	190	120
		ZP	-56	-2	-6	-18
0.5	H2SO4 100%	pH	7.4	4.0	4.4	5.0
		Cond	105	610	180	130
		ZP	-54	-3	-8	-16

Decanted sample contains 23% solids by weight. Tetrasodium pyrophosphate
was added 16 hours before the test started. After acid measurement taken
10 minutes after the acid was added. Filter cake and dried product was
diluted with distilled water to 23% solids prior to centrifuging and measurement
which was the sample density prior to filtration.

There are some deviations from plant practice; the sodium pyrophosphate
addition was only 0.5 lbs/ton to make up for the amount assumed lost in decant
water, and the acid addition was 2 lbs/ton to increase the effect of the acid.
Sulfuric acid was used on a pound-to-pound basis compared to 37% HCl. The
sulfuric acid pH became rather low and no direct comparison is possible.

The large acid addition did change both pH and zeta potential strongly. Both values are much lower than in the plant while the conductivity is comparable. The last fact can be explained by the pulp density which is lower in this sample than it is in the plant.

The advantage of the laboratory run is that it is possible to maintain constant conditions during the whole test. Especially was this true for pulp density where filter cake and dried product could be given the same density as before filtration. We can easily see that the zeta potentials have the lowest negative value after acid addition and that the negative value increases with acid removal by filtration and drying. The test failed to reveal any difference between HCl and H_2SO_4 that could not be explained by differences in amount of acid added.

Another test was designated to demonstrate the effect of tetrasodium pyrophosphate. Three series were run, one with pyrophosphate alone, one with pyrophosphate and 0.5 HCl lbs/ton, and one with pyrophosphate and 1.0 HCl lbs/ton. The results are shown in Figure 3. The zeta potential is given as a function of sodium pyrophosphate addition. It is a clear minimum in zeta potential in the range 1-2 lbs/ton of pyrophosphate, fairly independently of acid addition. The optimum amount for good dispersion is apparently the one presently used. (The sodium pyrophosphate was also in this case added after decantation and only half the nominal amount was used.)

pH values in all tests after acid addition has been lower than recorded in the plant. Recorded negative zeta potentials has therefore also been lower.

A look at the stochimetry of the additions might clear things up at this point. One lb of tetrasodium pyrophosphate with a molecular weight of 446 grams (including crystal water) equals 1.02 moles of phosphate ions or 4.08 sodium ions. One lb of hydrochloric acid 37% strength, molecular weight 36 grams equals 4.66 moles. The plant operation do, by use of those quantities, arrive at a pH around 6.6. Table 2 shows that dilution of the sample do not change the pH to lower values. The assumption that half the sodium pyrophosphate added is discarded with the decant water might be wrong. Most of the sodium ions could be strongly adsorbed on the mica surfaces and follow the solid phase. The conductivities of the settler under and overflows are lower than expected when the ions present in the water are considered. This indicates that an extensive adsorption has taken place. The hydrochloric acid will therefore do little more than neutralize the sodium ions.

Finally, a test series was run to evaluate the use of different acids. The combined use of both pyrophosphate and acid increased experimental errors and acid was therefore used alone. Tried were HNO_3, HCl, and acetic acid as monovalent acid, H_2SO_4 as divalent, and H_3PO_4 and citric as trivalent. Acetic, citric, and phosphoric acids are rather weak acids while the others are strong. The zeta potential was measured for different amounts of acid addition for each acid. The results can be shown many ways and this is done in Figures 4-6. In Figure 4, we see the zeta potentials of the mica as a function of acid addition in lbs/ton of acid of commercial strength. Seventy per cent HNO_3 changes the zeta potential most strongly followed by 37% HCl. One hundred per cent H_2SO_4 is not much different from HCl.

Figure 5 shows the same thing on a pH basis. We see that the trivalent acids give definitely less change in zeta potential with pH than do the others. The divalent and H_2SO_4 might also be a little less efficient than the univalent. HNO_3 might be more efficient than the other, but the difference is small. Acetic acid is seen to be quite efficient on a pH basis, but the quantities used are large.

Figure 6 shows the zeta potentials as a function of the most comparable factor, the acid concentration in pulp in terms of normality. HNO_3 and HCl are here close, while H_2SO_4 is somewhat less efficient. The weaker acids give much less effect.

CONCLUSIONS

If we accept the idea that a decreased number value of zeta potential gives a better filtration, then the acid of which we have the lowest consumption to decrease the zeta will be the best. In the present work, strong univalent acids are shown to be superior to others and HCl and HNO_3 almost identical. The drop in pH during normal plant operation is rather small. This pH range is not well represented on Figures 4-6. The conclusions about the ranging of acids has therefore to be based upon interpolation.

The effects of the acids added to the slurry should be twofold:

1) Neutralize the sodium ions from the pyrophosphate. All acids should here be equally effective as long as they do not get adsorbed on the mica surfaces. This will probably happen to the organic acids and to the tri and divalent acids to some degree.

2) Lower the pH of the solution. The strong acids will here be most effective as long as they are not adsorbed on the mica.

HCl and HNO_3 should be equally good and better than other acids. Both will in addition partly evaporate in the dryer in contrast to H_2SO_4. HCl is known to be corrosive to the dryer and whether or not HNO_3 will be any better can hardly be known without trial.
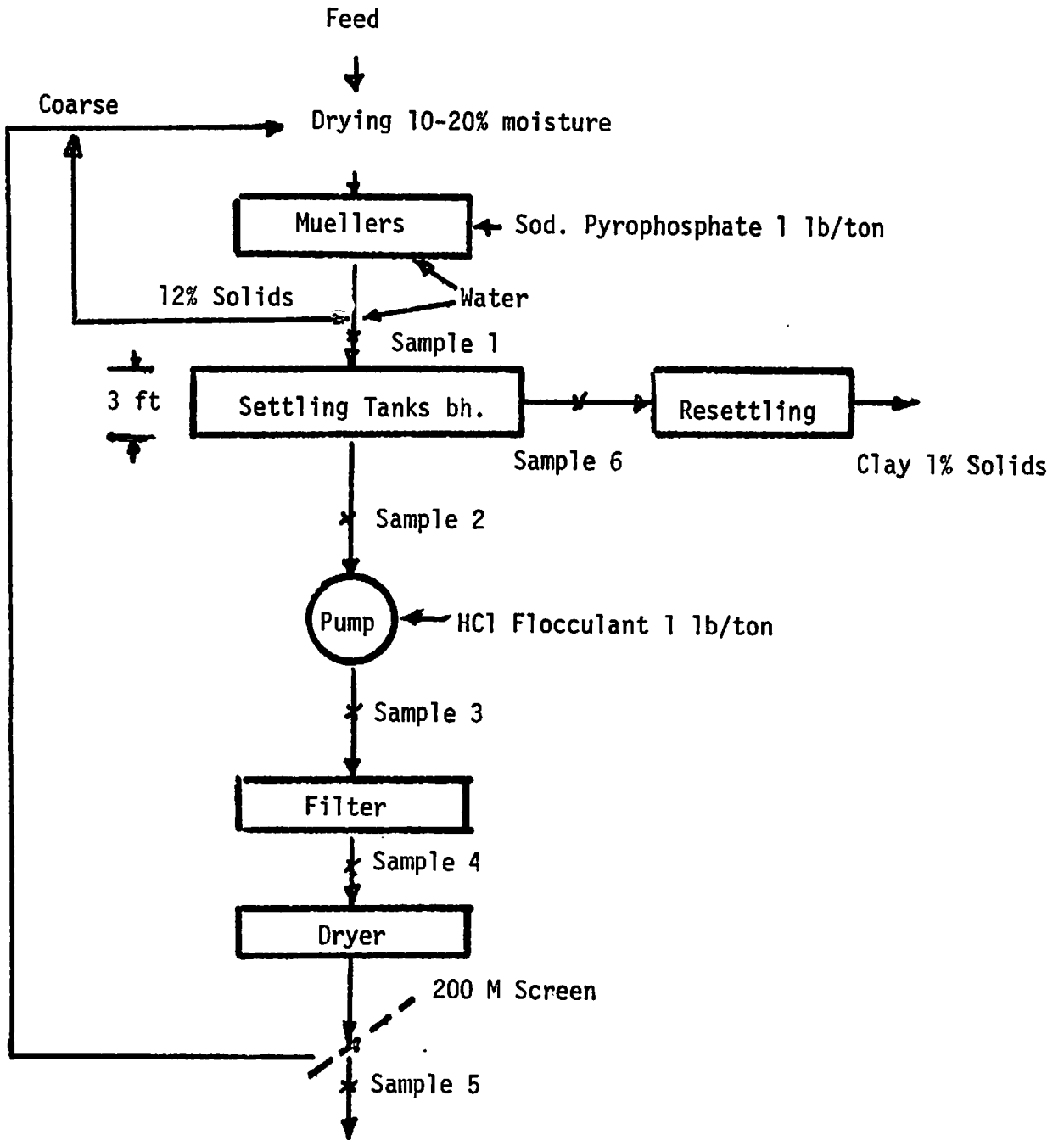
Feed

Drying 10-20% moisture

Coarse

Muellers ← Sod. Pyrophosphate 1 lb/ton

12% Solids   Water

Sample 1

3 ft

Settling Tanks bh. → Resettling →

Sample 6   Clay 1% Solids

Sample 2

Pump ← HCl Flocculant 1 lb/ton

Sample 3

Filter

Sample 4

Dryer

200 M Screen

Sample 5

Figure 1. Sample sites Diamond Mica Company.
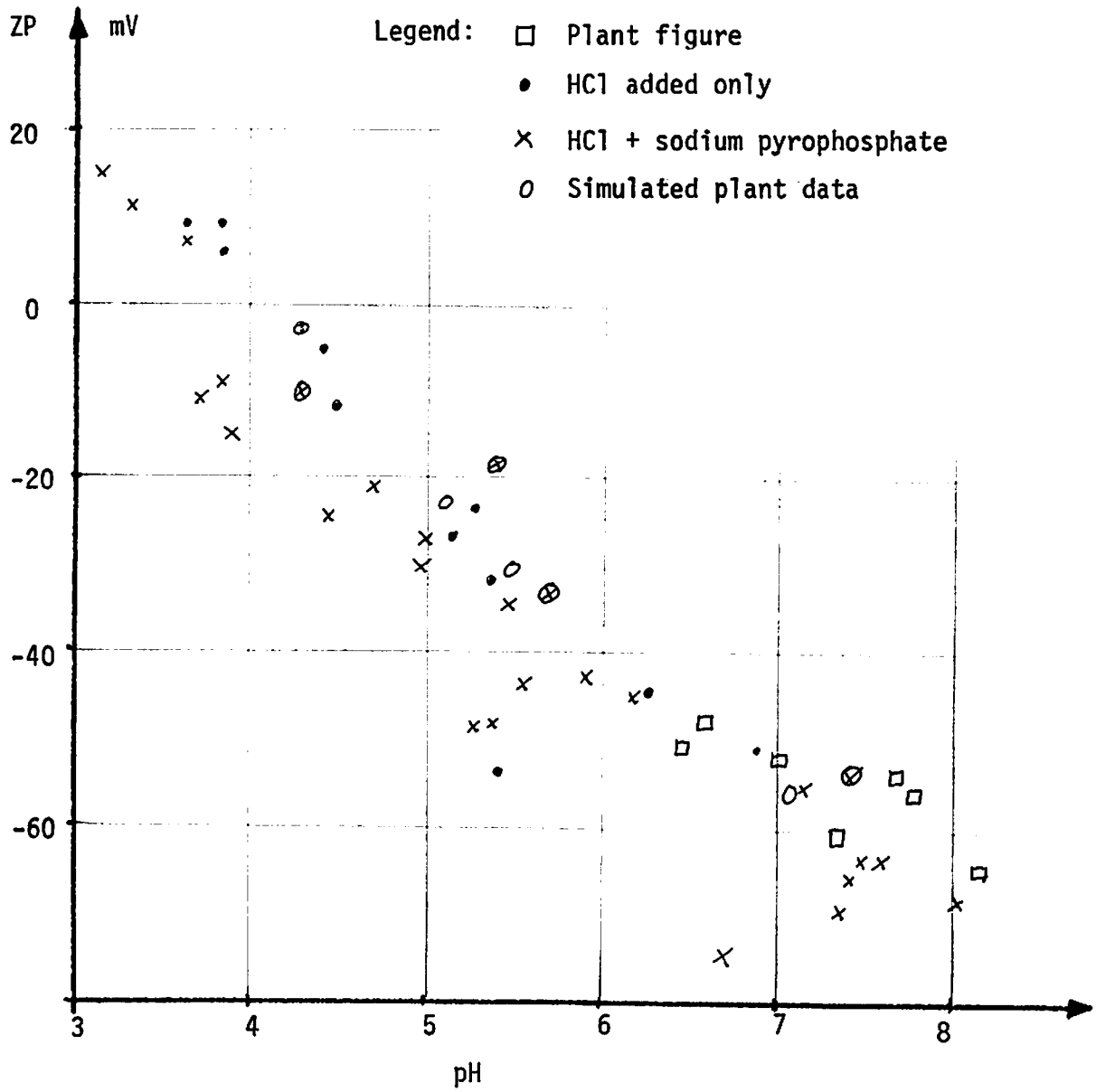
Figure 2. ZP as function of pH for mica slurries in pulps
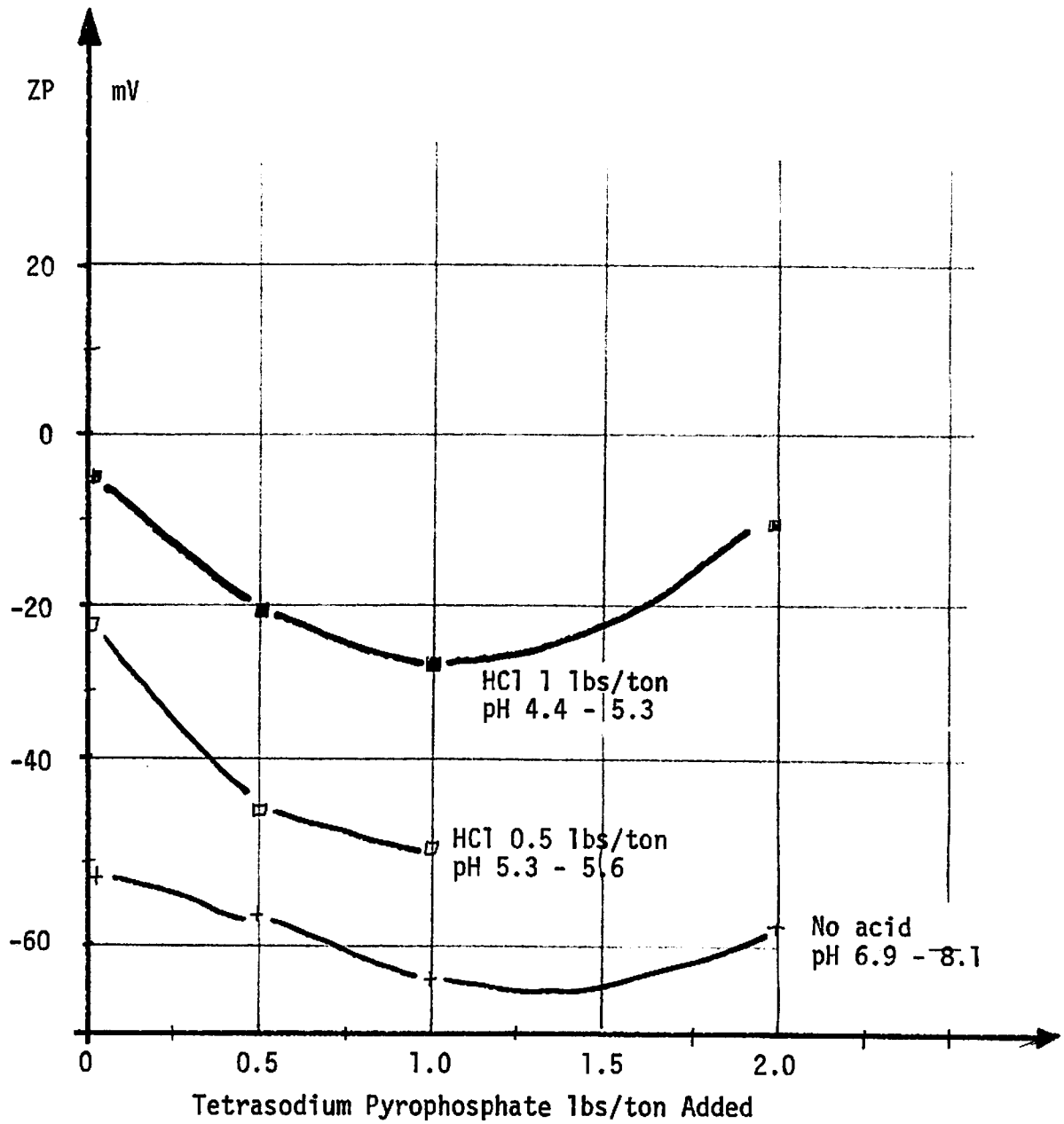that may contain HCl or sod. pyrophosphate.

Figure 3. Effect of concentration of tetrosodium pyrophosphate upon zeta potential of decant underflow at various acid additions.
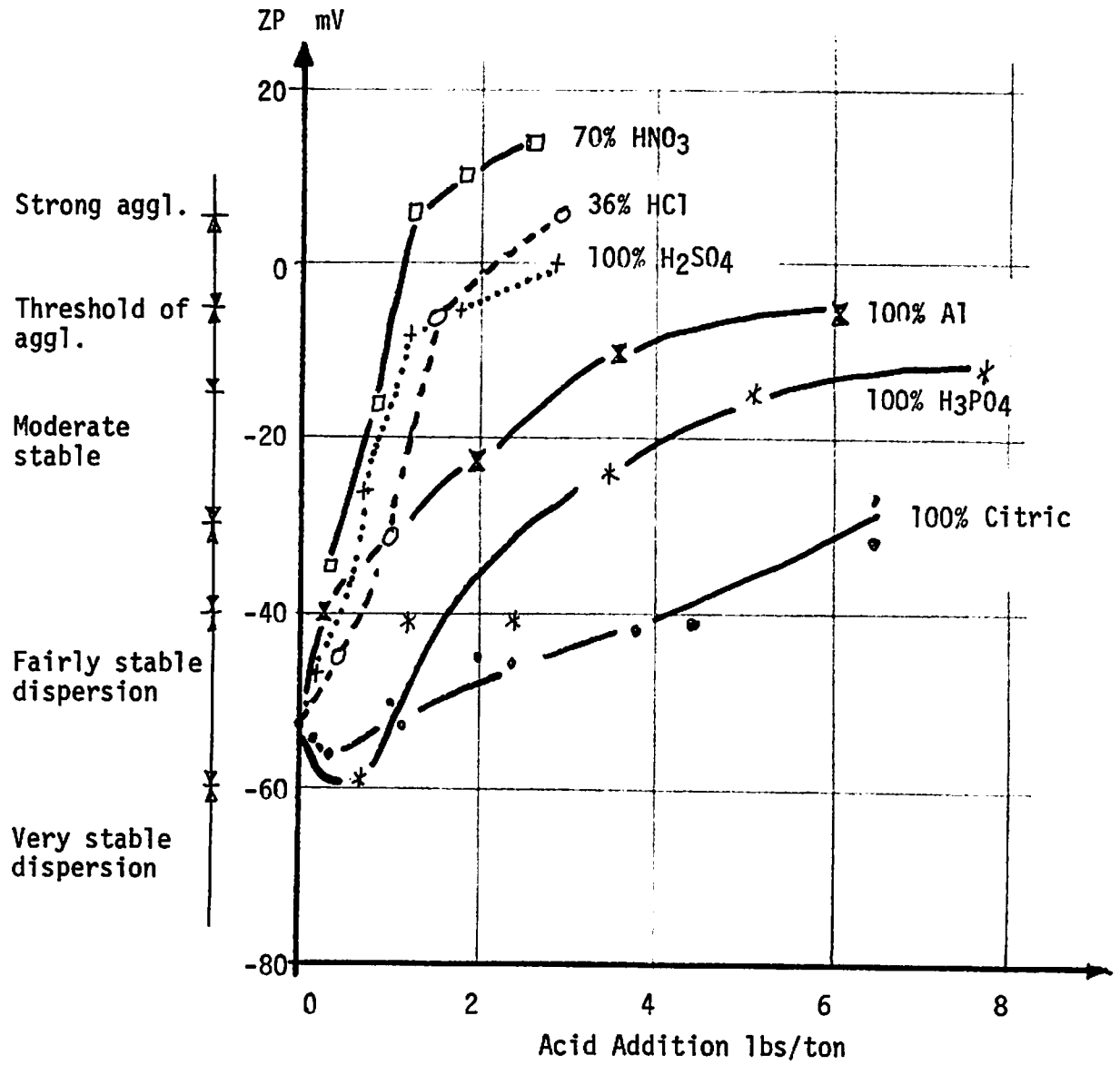
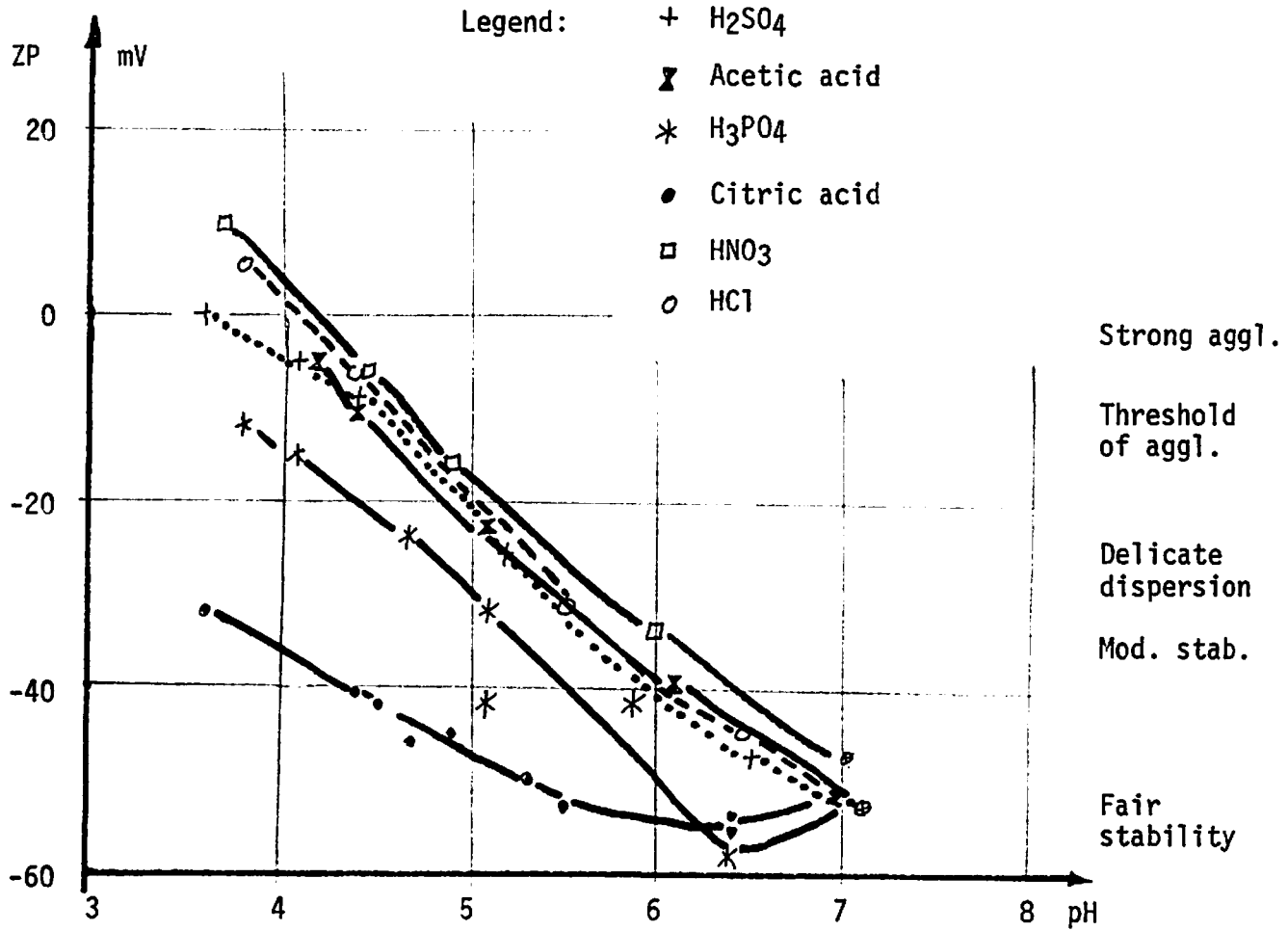Figure 4. Zeta potential of mica as function of acid addition in lbs/ton.

Figure 5. Zeta potential of mica as function of pH.
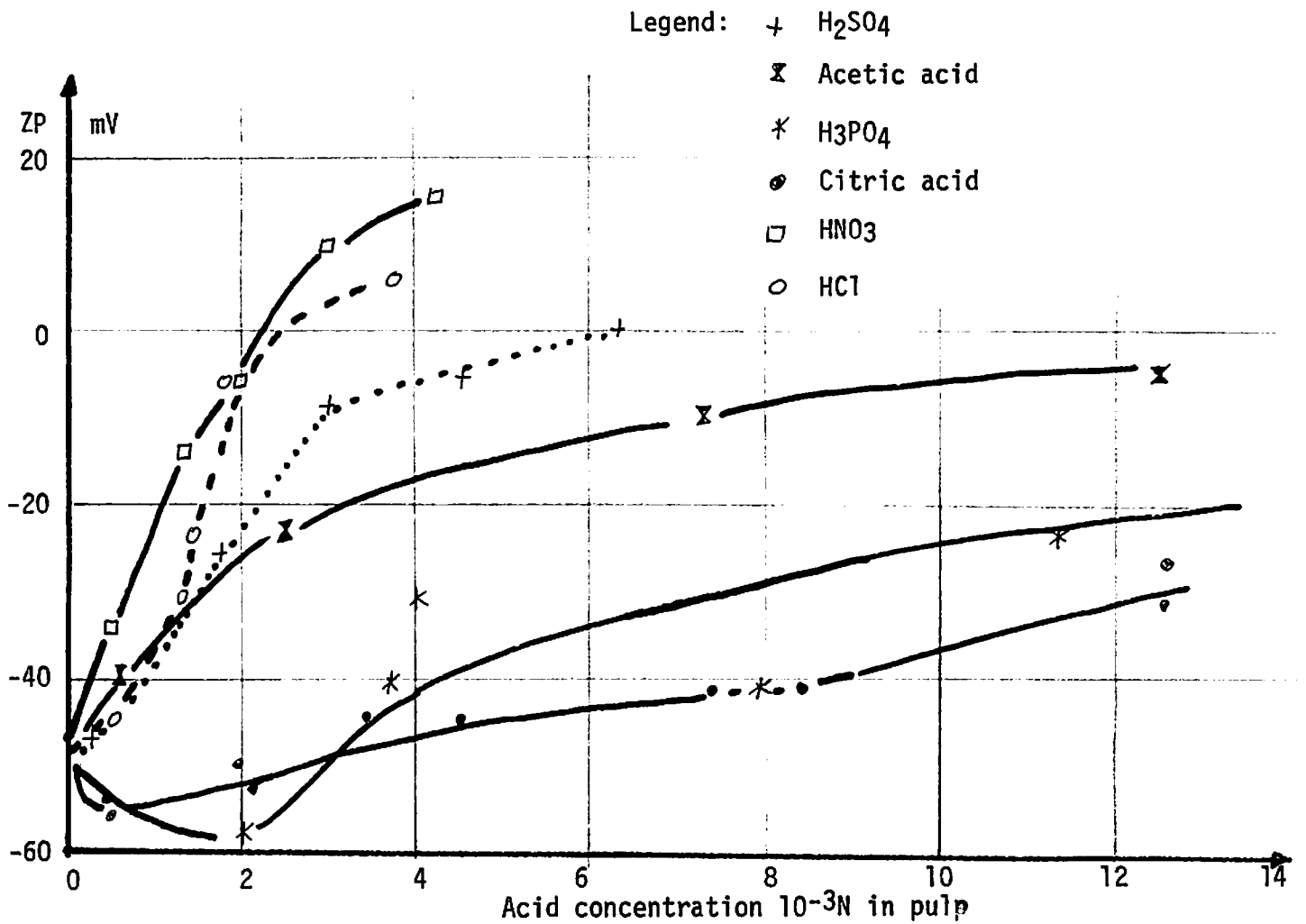pH is adjusted with different acids.

Figure 6. Zeta potentials of mica as function of acid normality. pH is adjusted
with different acids.