

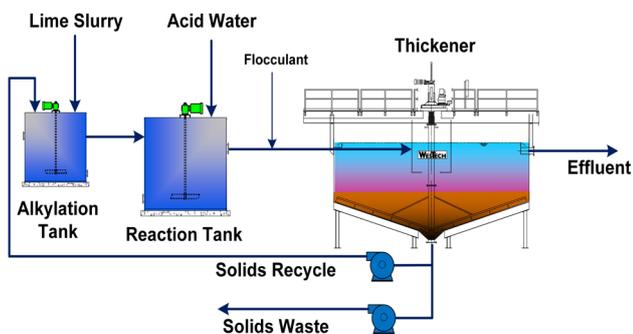
# NEUTRALISING ACID WATER

**Harley Schreiber, Jeff Easton, WesTech Engineering Inc., USA**, discuss HDS process technology for acidic water treatment applications.

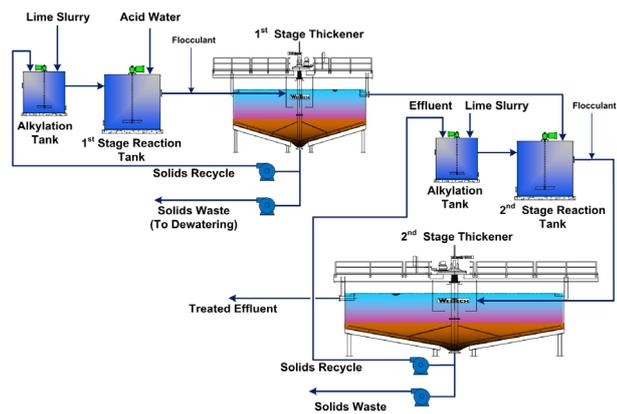
**T**he most common phosphate production process is a wet process that uses sulfuric acid to digest phosphate ore. For typical phosphate ores, this process generates approximately 5 t of calcium sulfate, referred to as phosphogypsum, per tonne of  $P_2O_5$  production. The insoluble phosphogypsum is typically separated from the product phosphate liquor using vacuum filtration with counter current washing (CCW). The washed phosphogypsum contains 20 – 25 wt% moisture and is either dry stacked or reslurried and pumped to storage. In either case, through compaction and rain water runoff, large quantities of water accumulate and are subsequently returned to the process.

Although the CCW washing process recovers the vast majority of the product phosphoric acid, accumulated water in the gypsum stacks is still very acidic, with a pH in the range of 1 – 2. In addition, the water has significant contaminants including sulfate, silica, arsenic, and other heavy metals. One of the major contaminants is fluoride which can be at levels in the range of 6 g/l and often found in the fluorosilicic acid form. In addition to the fluoride, phosphorous at similar levels contributes to the acidity of the water.

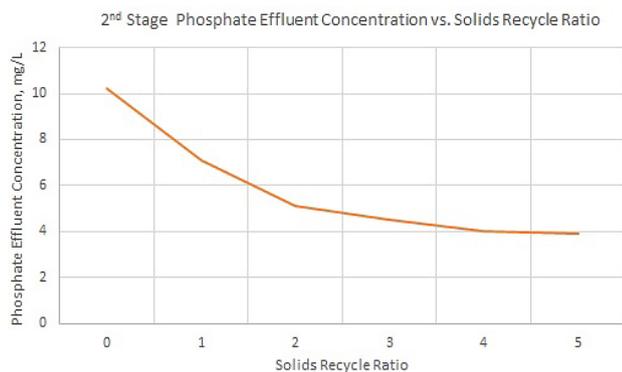
Treatment of any wastewater discharged, which may include provisions for gypsum stack closure, must include fluoride removal and acid neutralisation prior to discharge. The most common method for removal and neutralisation is through a two-stage lime treatment<sup>[2]</sup>. In the first stage the water pH is increased to about 5 with the addition of CaO or  $Ca(OH)_2$ . Here most of the fluoride is precipitated as  $CaF_2$ . This treatment stage also precipitates other contaminants such as metal hydroxides. Many of these contaminants are more soluble at higher pH, so solids must be separated from the treated water prior to the second stage neutralisation or risk resolubilisation. In the second stage of treatment, lime is again added to raise the pH to at least 9 for the removal of most of the phosphorous and a small amount of the remaining fluoride. If the ammonia content is elevated, a final pH of about 11 is required for its subsequent removal by air stripping<sup>[2]</sup>.



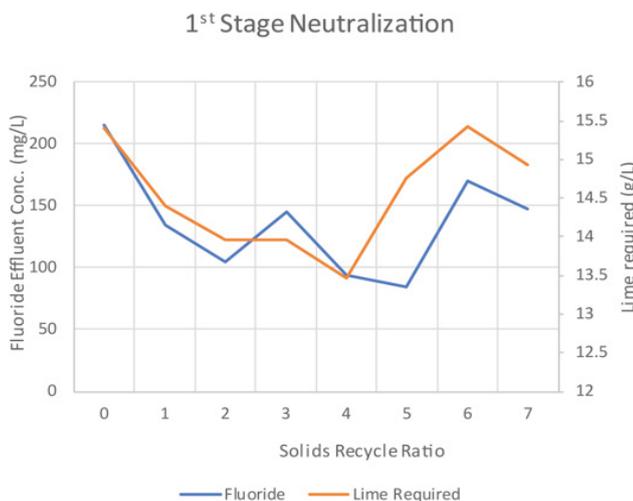
**Figure 1.** Typical single-stage, high-density sludge (HDS) neutralisation process.



**Figure 2.** Two-stage HDS neutralisation.



**Figure 3.** Effect of solids recycle on effluent phosphate concentration.



**Figure 4.** Lime requirement and fluoride effluent concentration versus solids recycle.

The high-density sludge (HDS) process is a proven technology developed for the neutralisation of acidic wastes and precipitation of metals from industrial discharges. Precipitation kinetics and particle formation dynamics are enhanced by seeding the precipitation reaction with densified and activated recycled solids. The HDS process produces final precipitates that are significantly higher in density than those which can be produced in a typical once through neutralisation/precipitation reactions.

WesTech Engineering, Inc. has experience in the application of lime treatment systems using the HDS process for metals removal from both acid rock drainage (ARD) and other industrial acidic waters. In a logical progression, WesTech has applied the HDS process and explored its benefits in the treatment of gypsum stack waste water. These opportunities include both laboratory bench scale testing and full-scale installation applications.

Figure 1 shows a simplified configuration of a typical HDS system. In the HDS process, precipitated solids are concentrated in a gravity thickener. Thickened solids, referred to as underflow, are continually recirculated to an alkylation tank where they are mixed with fresh lime slurry. Underflow is also periodically wasted from the circuit to balance the mass of solids precipitated from the incoming acidic water. After alkylation, fresh acidic water is reacted with the conditioned lime/underflow slurry in a separate reaction tank. To improve settling/separation characteristics, polymeric flocculant is added either directly to the slurry or to a separate flocculation tank designed to promote optimum floc growth. The quantity of underflow solids recycled (recycle ratio) in the system and mixing times required are determined through laboratory or pilot testing. Depending on the water being treated, the HDS process may include additional neutralisation stages and oxidation/reduction steps.

The fundamental objective of the HDS process is to provide conditions where solids precipitate onto previously formed solids, resulting in the growth of larger precipitates which have improved compaction properties. One way the HDS process provides this “seeding” for particle growth is through the recirculation of previously precipitated solids. A key consideration of the HDS process is that the lime slurry is combined with the recirculated solids in a separate reaction vessel (alkylation tank) prior to the addition of fresh acidic water. As such, it is presumed that the newly added lime coagulates coats the recycled particles ensuring the subsequent precipitation will occur on the continually growing particles (Aubé, 2004).

It is recognised that the HDS circuit also provides improved lime use efficiency. Any unreacted lime solids will settle in the thickener. Recirculating lime solids provides additional opportunity for reaction with the fresh acidic water.

WesTech Engineering has conducted several extensive laboratory neutralisation test programmes on phosphate gypsum stack waste water. Performance of an HDS circuit was the focus of each of these programmes. A summary of the key findings in three of these investigations follows:

### Case study 1

The first investigation was related to the design of an emergency neutralisation system for a gypsum pile water management system. Initial laboratory bench scale tests were completed with a waste acid sample containing about 4000 mg/l fluoride and 4800 mg/l of  $P_2O_5$  (2100 mg/l phosphorous). The configuration tested in the laboratory and ultimately the design for the full-scale system is shown in Figure 2.

In these tests, lime was added to control the pH to just under 5 in the first stage and about 9.5 in the second stage. It was determined from bench testing that at these pH conditions and a solids underflow recycle ratio of 5, a first stage underflow concentration in the range of 30 – 34 wt% could be achieved. In the second stage, although underflow concentration was improved by solids recirculation to about 5 wt% solids, the large quantity and naturally poor settling phosphorous solids makes it impractical to recirculate at a ratio of more than about 0.5 – 1. The residual fluoride concentration achieved in the bench testing was less than 40 mg/l after the first stage of treatment and less than 2 ppm after the second stage of treatment.

The bench test results proved to be quite accurate in prediction of full-scale performance. Upon start-up of the full-scale system, final effluent fluoride and phosphate concentrations were well below specification at about 6 ppm  $P_2O_5$  and less than 2 ppm fluoride. Excellent thickener underflow concentrations were also achieved with an average of 30 wt% solids in the first stage and 11 – 15 wt% in the second stage, which was considerably higher than predicted in bench tests.

### Case study 2

A second test programme with sample from another site, the benefits of applying the HDS process for two-stage neutralisation was again demonstrated. In this case, the owner was already utilising a two-stage, once-through neutralisation process, with the first stage pH raised to about 5 and the pH of the second stage operating at 11 – 11.5. WesTech conducted a bench test programme to determine the benefits of adding thickeners to the treatment process as well as determining the expected benefits of incorporating an HDS system.

WesTech has developed a thickener bench testing procedure that accurately predicts expected full-scale thickener underflow concentrations and thickener sizing requirements. A “unit area” sizing is generated from the test results. Unit area defines the thickener cross sectional area needed per tonne, per day of solids processed. These settling tests were conducted with samples generated with no solids recycle and also with a sample prepared by simulating the HDS process with 5 solids recycles. The required unit area was in the range of 0.14 m<sup>2</sup>/tpd of solids for the sample with no solids recycle and 0.12 m<sup>2</sup>/tpd with 5 solids recycles. The final underflow concentration predicted from these tests for once-through precipitation was about 14 wt% solids while with 5 recycles with the HDS process, a much higher concentration of 24 wt% was achieved. Although a slightly smaller unit area was predicted when using the HDS process, the increased solids loading required would result in the need for a larger thickener. The tradeoff of a larger thickener versus the benefits of significantly reduced sludge volume must be evaluated when considering whether or not to incorporate a HDS system.

Jar tests were completed simulating the second stage of neutralisation using once-through neutralisation as well as HDS tests with up to 5 recycles. Feed to the second stage of neutralisation was effluent from tests of first stage neutralisation that simulated a HDS system with a recycle ratio of 5. In this case, fluoride concentration in the first-stage effluent as well as the concentration of phosphorous in the second-stage effluent improved with each successive recycle. Figure 3 shows this relationship for the second-stage neutralisation.

Bench settling tests were also conducted with the second stage solids to quantify the expected underflow concentration relative to recycles. In this case, the predicted underflow

concentration went from 3.2 wt% with no recycle to about 5 wt% when using 5 recycles. In this case, the thickener unit area decreased from about 12.5 m<sup>2</sup>/tpd with no recycles to 7.5 m<sup>2</sup>/tpd with 5 recycles. As with the first stage thickening, although the unit area is decreased, the increased solids loading would require a larger thickener if using the HDS process.

### Case study 3

A final test simulating a two-stage HDS process was completed on another phosphate wastewater, this time with initial pH of 2.2, a fluoride concentration of about 3000 mg/l, and phosphate concentration of about 5000 mg/l. Jar tests were completed simulating the first stage neutralisation with a pH of about 5.3. The required lime dosage and fluoride concentration were measured after each successive solids recycle of the HDS simulation. The results of these two variables versus solids recycle ratio is shown in Figure 4. Final fluoride concentration and required lime dosage mirrored each other and were minimised at about 4 – 5 solids recycles. Performance relative to these parameters diminished at recycle rates greater than this.

These results again support claims of improved reaction performance with the HDS process. In addition, the reduced lime usage with 5 solids recycles supports a general claim that lime usage is optimised when using the HDS process. Results of 2-L settling tests predicted an increase in expected underflow concentration with increasing recycle ratios. The expected full-scale underflow concentration when using 0, 2, and 5 recycle ratios was 36 wt%, 38 wt%, and 44 wt% respectively. However, thickener unit area sizing was in this case, not improved with increased recycles. Therefore, as with the previous test, because of the additional solids that must be processed with the HDS, benefits of improved underflow concentration must be weighed against the larger required thickener area.

Second-stage HDS neutralisation tests to a final pH of about 12.1 were also completed in this test programme. However, as with previous tests, the benefit of the HDS system is less evident. In this programme, underflow concentration was only improved from 11 wt% with no recycle to 13 wt% with 1 or 2 recycles.

### Conclusion

With the potential for treating very large volumes of acidic waste water, achieving the highest possible thickened sludge concentration is imperative to reduce ultimate disposal costs. The HDS process is a proven technology in numerous acidic water treatment applications and is applicable to phosphate waste water as well. Additionally, this process is important in achieving maximum reaction rates, minimum effluent contaminant concentrations, and maximum lime utilisation. Despite the expected applicability to most phosphate waste water streams, there is sufficient variability among different sites that bench or pilot testing for each application is warranted. **WF**

### References

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