ABSTRACT

The surface chemistry of most minerals is affected by pH. In general most minerals develop a positive surface charge under acidic conditions and negative charge under alkaline conditions. Since each mineral changes from negatively charged to positively charged at some particular pH, we can manipulate the attractions of collectors to their surfaces by adjusting the pH.

pH Control is very critical in the flotation plant operations. Proper pH control will result in higher product yield, reduces reagent consumption and reduces operating cost. The condition of the froth is directly depended on the pH and it is controlled by regulating the flow of lime slurry to maintain the pH within the acceptable range.

In most of the sulfide flotation systems the pH is controlled by regulating Calcium hydroxide flow into the process. It is very critical to have a good quality and consistent lime slurry to have proper control of the pH in the flotation process. The quality of Ca(OH)₂ depends on the slaking process and hydration parameters like water/lime ratio, slaking temperature and agitation rate. A proper slaking process will cause an increase in particle surface area and create uniform particle distribution. This will result in higher reactivity and slower settling rate than Ca(OH)₂ generated by “Drowning”.

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INTRODUCTION

The effect of pH on the froth flotation is well known; the pH controls reagents or chemicals like calcium hydroxide also acts as modifiers. pH has very complex effects on the flotation process, particularly the way it changes how a particular collector adsorb on the mineral surface. Hence it is possible to manipulate the attraction of collectors to mineral surfaces by pH control. When Ca(OH)₂ dissolves it contributes calcium ions that adsorb onto the mineral surfaces. It is also a strong alkali, hence most widely used in controlling the sulfide flotation process. It is paramount that high quality and consistent density lime slurry is required for proper control of flotation process.

pH plays a very important role in the flotation process. At lower pH, Xanthates will decomposes back to its reactants. Also the surface chemistry of most minerals is affected by pH. Most minerals develop a positive surface charge under acidic conditions and negative charge under alkaline conditions. Since each mineral changes from negatively charged to positively charged at some particular pH, we can manipulate the attractions of collectors to their surfaces by adjusting the pH. The adsorption of the Xanthate ion to the mineral surface is also a function of pH.

pH Control is very critical in the flotation plant operation, proper pH control will result in:

- Increase in product yield
- Reduces reagent consumption
- Reduces the operating cost

In most of the sulfide flotation systems the pH is controlled by regulating the Calcium hydroxide (Modifier) addition into the process. Since pH measurement is logarithmic in nature, a unit change in pH will cause tenfold change in the load (ion Concentration). It is very critical to have a good quality and consistent lime slurry density to have proper control of the pH in the flotation process.

Several factors affect the proper functioning of a pH Control system, major factors are:

- Reactivity/Neutralization capacity of Ca(OH)₂
- Density of Ca(OH)₂ slurry
- Ability of the system to supply Ca(OH)₂ quickly on demand
- Reliable pH Measurement
- Flotation System Capacity & mixer design

Reactivity and the density are the two major issues that affect the day to day system operation. The other issues are mainly system design issues that are to be looked at during the design phase.

TEXT

Froth flotation is one of the most widely used mineral separation methods. It is also one of the simplest, economic methods to concentrate and separate valuable minerals from the ore. This process depends on the hydrophobic nature of the mineral. When air is bubbled though the slurry, hydrophobic minerals will attach to the bubbles and rise to the surface and form the Froth. The Froth is then removed for further treatment.

In sulfide ore flotation the efficiency of the process is mainly controlled by adding certain chemicals known as “Collectors” and by controlling pH (modifiers). Collectors are added to increase the hydrophobicity of the minerals. Collectors are organic compound that render selected minerals water repellent by the adsorption of molecules or ions on to the mineral surface. This reduces the stability of the hydrated layer separating the mineral surface from the air-bubble to such a level that attachment of the particle to the bubble can be made on contact (1). Xanthates are the most common Collectors used in the recovery of metal sulfides.
Factors affecting Reactivity/Neutralization capacity of Calcium hydroxide are:

- Quality of Lime (CaO)
- Slaking Process
- Storage & Handling of Ca(OH)\(_2\) slurry

**Quality of Lime**

The three primary factors that determine the quality of CaO are percentage of CaO available vs CaO content, soft or hard burnt lime and quantity of air slaked lime. Impurities and lower CaO content reduces the efficiency per ton of lime used. CaO produced from calcium carbonate of different composition, and Calcination method, will have different heat content.

They are generally classified as High reactive lime, Medium reactive lime and Low reactive lime.

Assuming that we need a 76.7°C (170°F) slaking temperature, we will require incoming water for slaking to have:

- 1.7 °C (35°F) for high reactive lime
- 10°C (50°F) for medium reactive lime
- 21.1°C (70°F) for low reactive lime

The heat content of these limes are indicated in the graph or chart below.

![Fig. 1 Heat content of various limes](image)
"Slaking" is a hydration process in which excess water is used for hydration of CaO and results in a slurry form.

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{Heat} \quad (1)
\]

Slaking process affects the surface area of calcium hydroxide particles formed and the surface area determines the rate of reaction. The higher the surface area correlates to higher capacity and efficiency.

High surface area is paramount because Ca(OH)_2 must dissolve to form hydroxyl ions before reaction. Such ionization takes place only at the solution interface on the particle (2). Higher surface area will result in less lime consumption when compared to lime with lower surface area or larger particle size.

The factors in the slaking process that affect the surface area of the crystals formed are ratio of CaO to water used for slaking, and the slaking temperature. Research has shown that slaking with excess water will result in a finer particle size of hydrates (4).

CaO hydration is an exothermic reaction. 1lbs of CaO will generate approx. 480 BTU of heat. Adding excess water can result in a drop in slaking temperature. Since temperature is the most important factor affecting the specific surface area, temperature control is essential for a uniform quality product (3). Slaking temperature can be maintained by controlling the slaking water inlet temperature or controlling the ratio of CaO to water. Proper agitation of the lime slurry during slaking process is also very important. A well designed mixer would ensure vigorous and continuous mixing at all the times during the slaking process. This enables the system to maintain a homogeneous mixture inside the slaker, breaking up lumps of fine agglomerated solids and improving heat & mass transfer. This will prevent localized overheating which will reduce the reactivity of lime. This also enables the system to maintain a higher uniform temperature during the slaking process.

Too little agitation will result in an uneven temperature within the slaking chamber resulting in hot and cold spots. The hot spots will result when slaking temperature gets over 100°C (212°F). Slaking at these temperatures will result in hexagonal crystals (5) of a large size and reduce surface area.

Once lime slurry is properly slaked it should be cooled below 48.5°C (120°F) to prevent the hydrate crystals from agglomerating with other fine particles of hydrates. Agglomeration of fine particle of Hydrates will reduce the surface area; hence the residence time in a slaker has to be optimized for the type of lime and slaking water quality.

The particle size distribution analysis of a properly slaked lime and regularly slaked lime is shown below.
Fig. 2 Particle size distribution analysis of properly slaked lime
Two slaking tests were performed using the same lime and water. On test “A”, the slaking water was heated to 24.9°C (76.8°F) and temperature rise was 48°C (118.4°F) which indicates a highly reactive lime. The second test “B” was done with same lime and water with initial temperature of 35.2°C (95.3°F) and temperature rise was 52.9°C (127.2°F). The second test showed an increase in temperature of 4.2°C (39.6°F) when compared to test “A”.

The lime sample was run according to method ASTM C110. The lime was pulverized to a top size near 6 mesh (3.35 mm), 100 grams of material was slaked with 400 ml of well water for 15 minutes.
Fig. 4 Slaking rate of lime – Test A.
Even though the temperature rise was not great, the impact on the particle size was noticeable. The graph "C" shows the particle size of hydrate particles for test “A” and “B”. The D50 particle size of test “A” was 10.24 µm and D50 for test “B” was 8.32 µm. The above test proves that by slaking lime at higher temperature the particle size of hydrate is
reduced, thus the specific surface of hydrate particle is increased which will result in a higher efficiency of neutralization and hence reduction in lime consumption.

Fig. 6 Effect of slaking water temperature – Test C1.
Fig. 7 Effect of slaking water temperature – Text C2.
Storage & handling of Ca(OH)2 slurry

Calcium hydroxide should not be exposed to an atmosphere high in CO₂. High CO₂ will cause spontaneous carbonation of calcium hydroxide suspension (6).

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \tag{2}
\]

Solubility of Ca(OH)_2 in water is very low and Hydrate crystals are suspended. Proper mixing should be provided in the storage tank to prevent agglomeration and settling. Fluid velocity should be high enough to prevent any settling in the pipes.

Consistency and/or density of lime slurry must be constant for proper pH control. Varying the density of the slurry will upset the pH and the control loop will never be able to attain steady state. This will result in the control loop to oscillate, which in turn will result in either overfeeding or underfeeding of lime. The slaker must be designed to maintain a constant slaking temperature between 76.6°C to 82.3°C (170°F to 180°F) and produce lime slurry with a constant density of 1.15 (20% solids). To achieve this, CaO and water must be added at a constant ratio and the temperature of the incoming slaking water must be controlled to maintain a desired slaking temperature. Further to compensate for the variation of lime bulk density and variations in the volumetric feed of quick lime, the lime feeder must be a galvanometric feeder with an accuracy ± 0.05%. A lime slurry density monitor is used to measure the density and control the ratio to maintain desired slurry density.

CONCLUSION

In most of the sulfide flotation systems the pH is controlled by regulating Calcium hydroxide flow into the process. It is very critical to have a good quality and consistent lime slurry to have proper control of the pH in the flotation process. The quality of Ca(OH)_2 depends on the slaking process and hydration parameters like water/lime ratio, slaking temperature and agitation rate. Proper slaking process will cause an increase in surface area and create uniform particle distribution which will result in higher reactivity, less lime consumption and a slower settling rate than Ca(OH)_2 generated by “Drowning”.
Reference:
(4) Factors Affecting Quick lime Consumption in Dry FGD, M. Hassibi. Chemco Systems, L.P.