

## DISPOSAL OF HYDROXIDE SLUDGE SOLIDS FROM ALUMINA, SMELTER AND FABRICATION PLANT EFFLUENTS

Rogers, M.G.

*Australian Process Technology Pty Ltd*

### Abstract

Aluminium and alumina operations, aluminium smelters, fabrication and anodising plants produce corrosive wastewater streams that contain dissolved aluminium salts and suspended solids. Neutralisation prior to disposal creates a gelatinous precipitate of contaminated aluminium hydroxide sludge. Separation, and disposal of this sludge must satisfy environmental protection requirements.

Many of these operations are located close to, or in heavily populated regions where aluminium is used as a building and construction material and in fabrication plants with anodising facilities for corrosion protection. This particularly applies to Europe, USA and Japan where the high cost of disposal of large quantities of hazardous sludge is a major environmental problem.

A process has been developed for converting the hydroxide sludge solids into large dense crystalline particles that can be thickened, filtered and recycled for disposal or re-treatment.

The technique involves chemical treatment and flocculation of the effluent in the presence of previously precipitated solids. Under specific conditions the changes brought about by the chemical reactions cause agglomeration, ageing and consolidation of the solids where the smaller particles disappear while the larger particles grow larger at an apparent higher density. These coarser particles settle faster, thicken to a higher underflow density and produce slurry with a higher filtration rate.

The procedure has application in the treatment of dilute liquor streams from alumina refineries, aluminium smelters, fabrication and anodising plants. The process, which partially converts aluminium hydroxide to gibbsite, can be applied to a wide range of metal hydroxides, including titanium hydroxide (rutile), iron hydroxides (goethite, hematite and magnetite), magnesium hydroxide (periclase) and mixed hydroxides.

### 1. Introduction

Alumina refinery effluent streams contain a low concentration of aluminium and other metals from liquor spills, plant wash down, mud stack drainage, acid washing, power house water, cooling water blowdown and rain water collection.

Aluminium smelter plant effluent streams contain aluminium as well as descaling and pickling chemicals. Fabrication, anodising plant and electroplating system effluents contain chemicals used in degreasing, etching, anodising, and a variety of rinsing operations. The major problem associated with treating anodising wastewater is the production of a large amount of aluminium hydroxide sludge. Because of its high moisture content, disposal of the sludge is often difficult and costly.

The wastewater from the above plants can range from acid (pH <2) to alkaline (pH >12).

Most environmental agencies maintain strict limits on the discharge of wastewater into containment ponds, rivers and estuaries. A typical specification is:

Component	Unit	Discharge limit
pH		6–9
Soluble Aluminium	mg.l <sup>-1</sup>	15 max.
Soluble Iron	mg.l <sup>-1</sup>	1 max.
Total Iron	mg.l <sup>-1</sup>	10 max.
Soluble Vanadium	mg.l <sup>-1</sup>	2 max.
Suspended Solids	mg.l <sup>-1</sup>	50 max.

Neutralisation prior to disposal creates a gelatinous precipitate of aluminium hydroxide sludge that settles slowly with poor compaction to an underflow solids concentration of 1 to 2%.

The seed recycle precipitation process involves flocculation and solids contact reactions in the presence of previously precipitated solids, to produce slurry containing larger crystalline aluminium hydroxide particles, which can be easily separated. This precipitation process consists of three steps:

- Agglomeration;
- Ageing; and
- Consolidation by thickening or filtration.

The consolidation process causes irreversible changes to take place that improves the ease of solid liquid separation. The fine precipitated solids are converted into relatively coarse hydrate solids that settle to a solids concentration of 20% or more. A slurry side stream can then be filtered for disposal or recovered for re-treatment to expel solids from the system and maintain the process in balance.

This process has been practiced for some time using reactor clarifiers, and other process equipment.

A feature of the seed recycle precipitation is that a minimum concentration of aluminium in the feed stream is not critical. The aluminium hydroxide acts as a coagulant, and freshly precipitated gel is deposited on the surface of existing larger diameter particles during the solids contact reaction.

There are also analogous operations in both municipal and industrial water treatment plants. In this case aluminium salts, lime, and soda ash are added to coagulate and remove fine clay solids or turbidity and produce potable or clarified water. The reactions are carried out at a pH between 5.5 and 8.5, at temperatures between 15 and 30°C.

**KEY WORDS:** aluminium hydroxide, precipitation, effluent, environment, pollution

## 2. Precipitation Mechanism and Kinetics

In a conventional alumina precipitation system, appropriate nuclei must be present to initiate crystal growth and a solution must be supersaturated with respect to the component to be crystallized for particle growth to occur. Supersaturation provides the driving force for crystal growth while the nuclei provide the low energy sites for solute deposition<sup>(2)</sup>.

Neutralization of the effluent to pH 6–9, results in the formation of an off-white gelatinous precipitate of aluminium hydroxide nuclei with a particle size between 0.01 and 0.02  $\mu\text{m}$  (10–20 nm). These primary nuclei agglomerate rapidly to form small clusters that attach themselves to the larger particles, expanding the structure and extending the particle diameter. These primary and secondary particles, having a diameter up to 0.2  $\mu\text{m}$ , form a low density suspension. Because of the fine solids this slurry still does not settle well and is difficult to separate by filtration.

In the seed recycle precipitation system the predominant mechanism for aluminium hydroxide crystal growth appears to be agglomeration of primary nuclei and small particles to form secondary nuclei. Many factors determine whether a collision will result in agglomeration, including particle size, relative velocity and orientation, particle morphology, surface condition and activity. Collisions between very small particles, less than 0.1  $\mu\text{m}$ , frequently result in agglomeration while collisions between large particles greater than 100  $\mu\text{m}$ , are seldom effective. Flocculation is an important factor in this process because it reduces the surface repulsion forces and binds the fine particles together. The increase in particle size at 20:1 recycle solids to feed solids is shown in Figure 1.

The recycle of previously precipitated solids is the major source of secondary nuclei that provides the active particle growth sites.

Since the sedimentation rate is directly proportional to the diameter squared (Stokes Law), the increase in sedimentation rate of the larger particles can be as high as 1000 times that of the smaller particles at the same density differential and liquid viscosity (Figure 2).

**Note:** Coagulation and Flocculation are precisely defined in this paper. Coagulation means the agglomeration of primary particles into a mass up to 500  $\mu\text{m}$  in diameter. Flocculation involves agglomeration as well as binding of small coagulated clusters into larger particles. Coagulation and flocculation increase the effective particle size, which in turn increase the sedimentation rate and the underflow concentration.

## 3. Laboratory Testwork

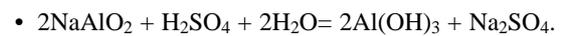
Experimentation is essential on each effluent to determine the most effective procedure for treatment and the expected quality of the clarified water.

### 3.1 Preliminary Evaluation

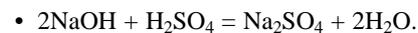
Preliminary tests include selection of the neutralization acid or alkali, followed by a survey of flocculant types, flocculant dosage, dispersion of the flocculant and appearance of the flocculi after initial mixing. The initial selection involves a simple straight-line sedimentation test and examination of the particles for size and shape under a microscope.

### 3.2 Reactions

The reactions involved are:-



Neutralization



Neutralisation

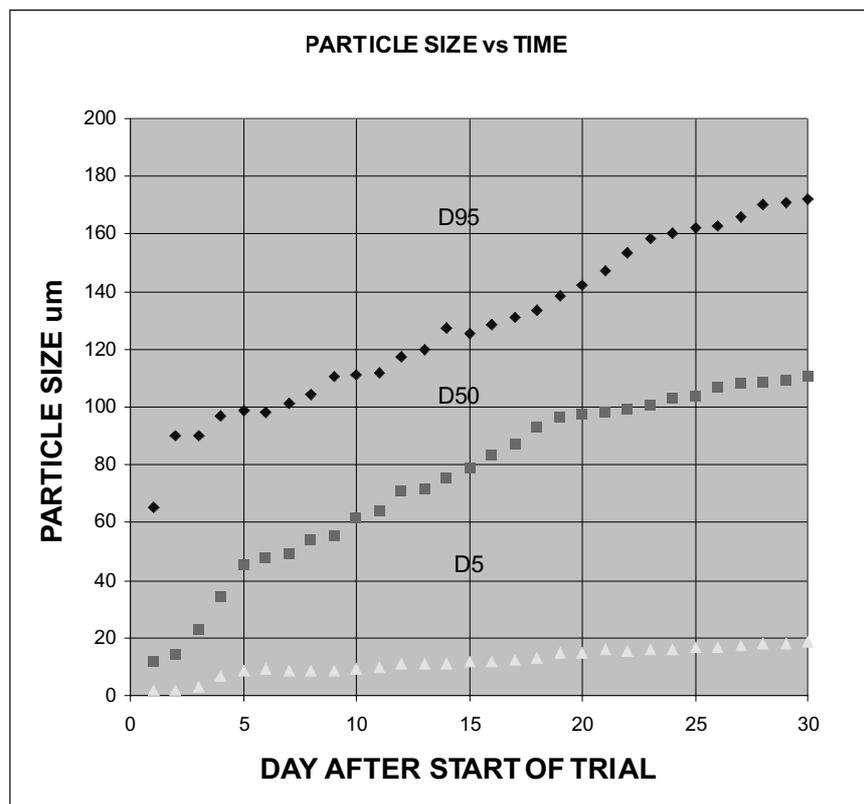


Figure 1 — D<sub>50</sub>, D<sub>95</sub> and D<sub>5</sub>, Average Particle Size Growth versus Time

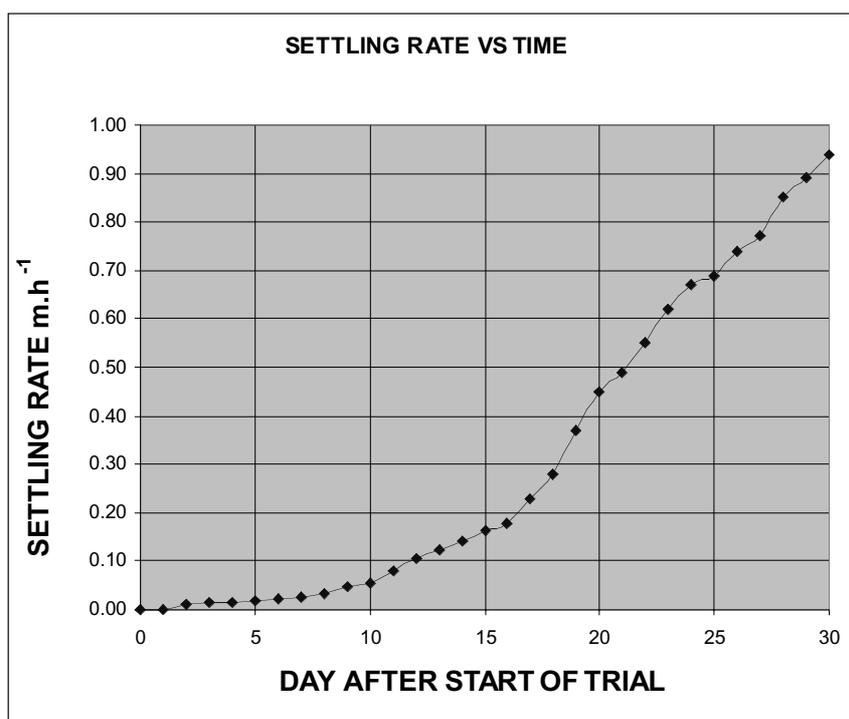


Figure 2 — Solids Settling Rate Growth versus Time

- $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{CO}_3$ .  
Neutralisation
- $2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{SO}_4 = \text{Al}_2(\text{SO}_4)_3 (\text{Alum}) + 6\text{H}_2\text{O}$ .  
Alum production

### 3.3 Process Variables

These include the mineralogical, physical and chemical properties of the solids, the solids and liquid density, particle size, liquid viscosity and temperature, solids concentration, flocculation characteristics, underflow concentration, surface activity, and the size and geometry of the containment tank.

The control variables that affect the operation include:—

- **Optimum reaction pH.** Surface charges are affected by pH. The pH range 6 to 9 is the most effective for precipitation and effective flocculation. The addition of lime as a final pH control often assists in the removal of heavy metals.
- **Flocculant Type and Dosage.** Most plants have performed surveys of flocculant types. It is almost impossible to operate without flocculant and a current in-process flocculant is preferred. Depending on the initial feed concentration the dosage varies between 10 and 50 g.t<sup>-1</sup>. Generally added as a 0.05% solution.
- **Reaction Time.** Initial tests are performed at 5, 10, 20, 40 and 80 minutes. Most metal hydroxide materials require agitation time between 10 and 40 minutes. The straight line-settling rate over 30 minutes is used to judge the effect of reaction time. The settling rate tends to increase even at long reaction times however the increase is marginal at reaction times greater than 40 minutes.
- **Chemical Addition.** Determine the quantity and effect of Lime as the neutralizing medium on acid effluents, the dosage of oxidant in the case of biological activity, and other Surface Activation compounds, etc.
- **Recycle Solids Rate.** To avoid extended periods for particle size growth, it is possible to use precipitated

TCA (Tricalcium aluminate) or very fine hydrate solids (less than 10  $\mu\text{m}$ ) as the initial seed. Coarse hydrate cannot be used because it does not collect the freshly precipitated hydroxides and settles independently. The recycle rate is directly related to the solids surface area and its activity. The recycle rate is determined by a mass ratio to the incoming solids rate within the range 10 and 30 times the precipitated solids mass in the neutralized feed.

- **Reaction Temperature and Time.** Reaction temperature and time have a significant influence on the property of the reaction products. The properties of the aluminium hydroxide sludge, such as sludge volume and moisture content, are minimised if the reaction temperature is kept above 40°C. This produces sludge with satisfactory dewatering characteristics. The neutralizing reaction should be performed slowly with additional heat supplied to the system as required.
- **Recycle Particle Size.** The flocculated solids are a loose assembly of smaller particles containing an appreciable amount of water. The water can be expressed from these flocs by thickening, filtration or centrifugation. This mass is then subjected to mild shearing forces to partially disperse the aggregates before recycling.

### 3.4 Quantitative Tests

These include batch and bench scale continuous tests. The process variables listed above are varied over the expected range and the effect monitored during the tests.

#### 3.4.1 Reactor Type and Sizing

The reaction stage batch tests are performed using a multiple mixer station with individual variable speed controls. Up to six tests using 1-litre beakers can be performed simultaneously.

After neutralization the flocculant is added over a period of 10 to 20 seconds with a high mixer speed. The

speed is reduced to mild agitation and the time for the appearance of floccules is noted. Reactor residence time is generally between 10 and 40 minutes.

### 3.4.2 Clarifier/Thickener Type and Sizing

The straight line-settling rate is determined over the first 30 minutes of the settling test.

The underflow concentration is determined from extended raked slurry samples (Figure 3).

Conventional design of a clarifier thickener involves four operations:

- Flocculation and mixing
- Clarification
- Zone settling, and
- Consolidation.

Each of these operations requires an area to perform its function effectively. In this treatment process the flocculation and consolidation operations have the most effect on the particle growth and this means that the conventional thickener raking blades are not effective in promoting particle growth. Recycling and ageing over a period of 24 hours indicates particles can grow to a diameter of 20  $\mu\text{m}$ . The recycle seed ratio and the underflow concentration against time are shown (Figure 4).

Thickener and Clarifier sizing procedures are described elsewhere.

### 3.4.3 Filter Type and Sizing

Pressure and vacuum filtration tests are performed on the Clarifier/Thickener underflow to determine the most suitable filter. The filtration rate will depend primarily on as the feed slurry characteristics, slurry concentration, filter cake disposal alternatives and other factors. Pressure and vacuum filtration sizing procedures are described elsewhere.

On site tests are essential for accurate and proper process design of the above equipment.

## 4. Pilot Plant Testwork

This involves recycling of the underflow from a small pilot plant over a period up to 5 weeks. Initially all solids are held in the thickener and reaction tank, with only clarified water discharged.

The pilot plant operation should be continuous with bench scale tests to confirm the process performance.

While all effluents show different characteristics, all of the factors listed below should be evaluated during the pilot plant phase. The full-scale plant design will require observations and quantitative data on any significant variations in the:-

- Reaction Time.
- Control and adjustment of pH
- Rate of increase in underflow concentration
- Effect of thickener raking design on the particle size and underflow solids movement
- Flocculant addition and dispersion rate.
- Settling rate using long or short retention times in the thickener feedwell
- Recycle seed solids ratio
- Reactor agitation intensity and period.
- Clarifier upflow rate and therefore the overflow clarity

## 5. Continuous Operation

The rate of increase in particle size is quite slow during the initial 10 days however this increases as the solids recycle rate is increased to 20 times the feed solids or more. The change in underflow concentration over a period of 30 days is shown (Figure 3).

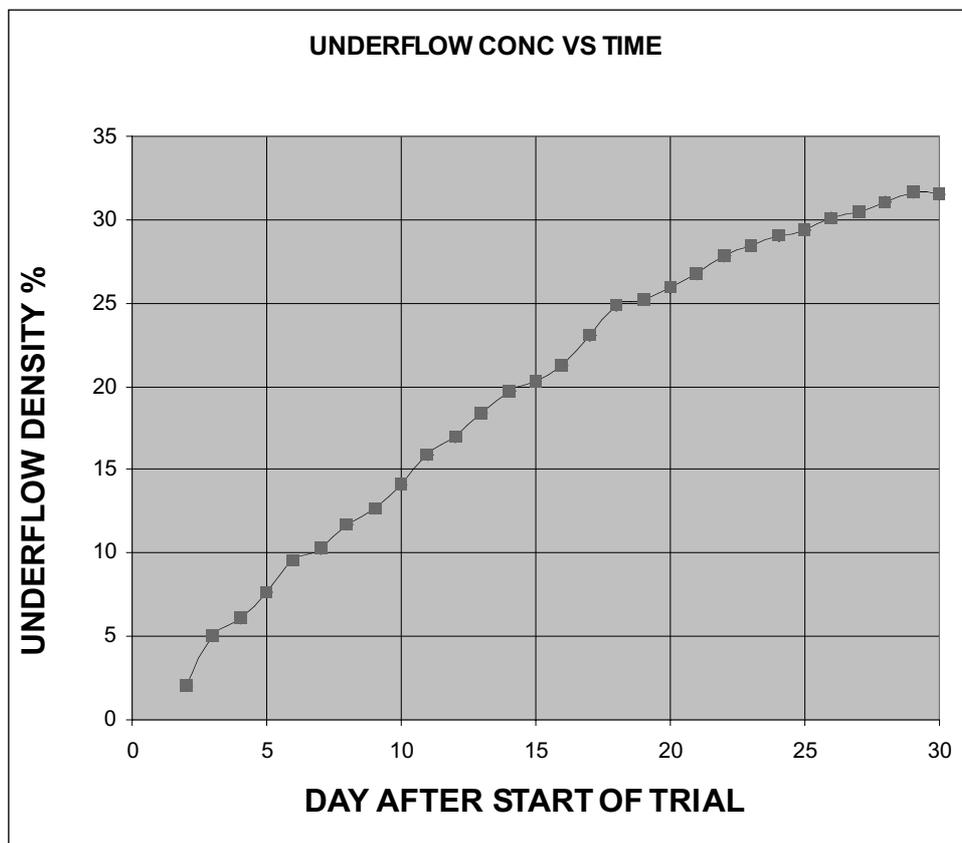


Figure 3 — Underflow Concentration versus Time

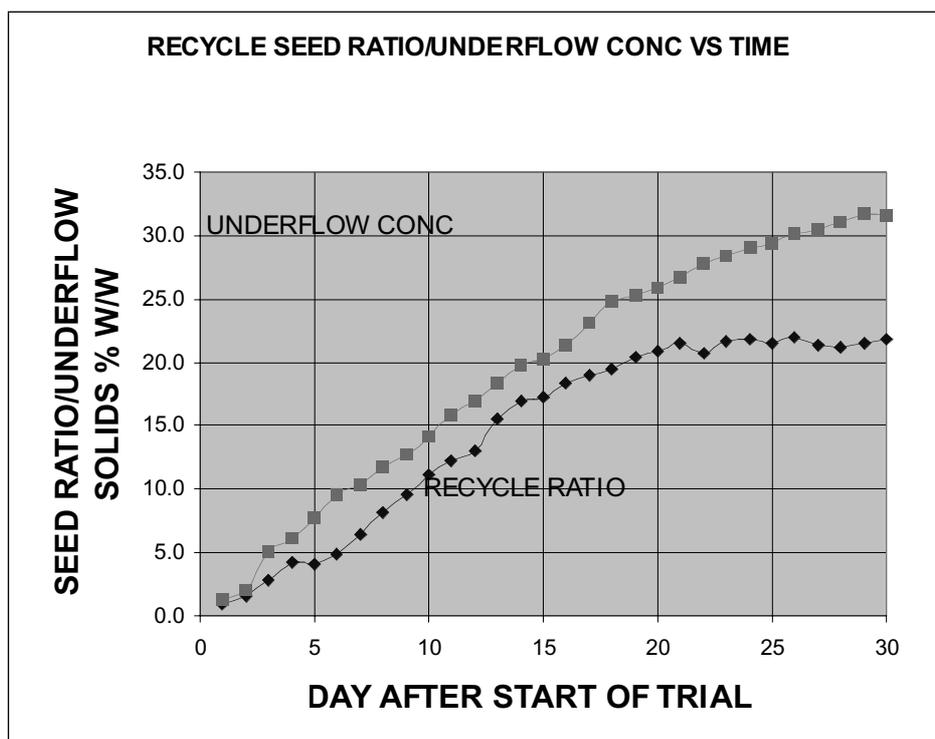


Figure 4 — Underflow Concentration &amp; Recycle Seed Ratio versus Time

Over a 5-week test period the sensitivity of the process to high step flow changes and chemical additions can be determined.

Every effluent is different and this affects the neutralisation and precipitation reaction conditions. Laboratory experimentation is essential before a process can be developed, and equipment selected and sized for the particular wastewater flow rate and conditions.

## 6. Conclusion

The seed recycle technique is effective in converting aluminium hydroxide sludge solids into large diameter dense crystalline particles that can be thickened, filtered and recovered.

Low-density voluminous hydroxide sludge that settles slowly with poor compaction to an underflow solids concentration of 1 to 2% can be converted into relatively coarse hydrate solids that settle to a solids concentration of 20% or more.

Initially a high solids surface area is required to maximise the reaction rate, followed by fast particle growth to

maximise the solids settling rate and thickener underflow density.

The predominant mechanism for aluminium hydroxide crystal growth appears to be by agglomeration of primary nuclei and small particles to form secondary nuclei. Secondary nucleation involves a physical interaction between two particles, where flocculation plays an important part in the process because it reduces the surface repulsion forces and binds fine particles together. The major source of secondary nuclei is the recycle of previously precipitated solids.

Accurate pH control, mild agitation, ageing, fine particle size, flocculation, a high seed charge and raking of the settled solids enhance coarsening of the solids in suspension.

## Acknowledgements

This paper is based on work performed for a number of alumina refineries, smelters and metal surface treatment plants in Australia and Europe. Their assistance is gratefully acknowledged.

## References

- Bisio, A. and Kabel, R.L. (1985) *Scale up of Chemical Processes*. 1st ed., New York, USA, Wiley-Interscience.
- Mullin, J. W. (1993). *Crystallization*. 3rd ed., Oxford, UK, Butterworth-Heinemann.
- Purchas, D.B. and Wakeman, R.J. (1986). *Solid/Liquid Separation Equipment Scale-Up*.
- Yoji Fukuyama, Yasunao Misaka, Kenji Kato (1978). *Recovery of Aluminium Hydroxide From Fabricating Plant of Aluminium Products*.
- Taiwo O Kayode, John Gregory (1988). *A new technique of monitoring alum sludge conditioning*.