PRECIPITATION PROCESSES IN THE TREATMENT OF INDUSTRIAL INORGANIC WASTEWATERS: IMPACT OF REACTOR AND PROCESS CONFIGURATION

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SUMMARY: VEOLIA implements several precipitation processes to treat various industrial wastewaters containing high concentrations of inorganic contaminants. The processes commonly used by VEOLIA include conventional precipitation and more advanced processes using some form of sludge recirculation in various flowsheet configurations and reactor designs. The reaction mechanisms and impact of hydraulics that are crucial to these processes are not always well controlled. Therefore, the objective of this work was to define the key parameters that affect the performance of these processes, identify potential improvements, and establish the application criteria of each process.

1. INTRODUCTION

The physicochemical treatment of aqueous byproduct streams from industrial operations typically involves chemical precipitation of the contaminants via acid-base neutralization (or other means) followed by separation of the solids from the solution. The separated solids are then dewatered and, depending on compositional value, may be optionally dried and recycled back to the source operation, an external market or simply disposed. The treated effluent is then either recycled or discharged. In some cases, additional treatment may be necessary to satisfy applicable discharge regulations.

The size, shape, and density of the precipitated particles can have a significant impact on the sludge rheology, settling rate, and dewatering performance.

For example, the solids produced in conventional precipitation processes generally have a low median particle size (D50) and wide particle size distribution (PSD) compared to more advanced precipitation processes. A low D50 manifests itself as sludge that is difficult to settle and dewater and may exhibit undesirable pseudoplastic or Bingham plastic tendencies. This can negatively affect the efficacy of recycle from a practical process or operational perspective and be deleterious to the quality and composition of the recovered solids in general.

Additionally, in a conventional neutralization plant, scaling due to saturated or metastable levels of constituents in the treated effluent can be problematic. Gypsum scaling is commonly observed (Adams J.F. and Papangellakis V.G., 2003). Processes that include solids recirculation back to the point of neutralization can reduce or totally eliminate scaling because the increased surface area fosters secondary nucleation and reduces the level of gypsum (and other constituent) supersaturation.

To resolve these problems, advanced precipitation and crystallization processes have been developed that address the science of particle formation and growth to improve the recovered solids properties. The production of a sludge with a relatively high settled slurry concentration (i.e., >20% by weight solids) distinguish the advanced precipitation processes from conventional treatment systems (Finn D., 1995). VEOLIA Environnement has developed and used advanced intensified precipitation processes (Cook R.G., 2003) with sludge recirculation (Muhr, H, Plasari E.2007) including :

- Forced-circulation, draft-tube crystallizers with custom mixers that yield very high circulation to minimize supersaturated zones. Theses reactors are often employed with some form of sludge recirculation.
- Classical agitated reactor.

Pilot-scale trials were conducted using acidic industrial wastewaters (sulphate and others) to characterize the impact of reactor design and process configuration on the overall process performance. PSD measurements reveal superior performance of a process involving sludge recirculation versus a conventional process. (as mentioned by Tapsell G., Prijadi J. et al.).

The production of a sludge with a nominally higher density (i.e., >20% by weight solids) distinguish these advanced precipitation processes from conventional treatment systems.

2. METHODOLOGY

2.1. Effluent characteristic

Pilot-scale trials were conducted utilizing industrial wastewaters to compare the performance of conventional precipitation to the more advanced technologies.

Table 1 presents the composition of the sulfuric acid wastewater used in this work.

Table 1. Sulfuric Acid Wastewater Composition.

H_2SO_4 g/l	SO_4 g/l	TSS mg/l	Fe mg/l	Ti mg/l	Cl mg/l
6.51	6.79	168.8	100	177.6	1220

2.2. Scaling determination

To assess gypsum scaling and the effects of sludge recirculation in the process, a slurry tank containing a known solids concentration was used to feed the precipitation reactor and control the solids concentration in it at 50 and 120 g/L. Blank sheets of material were placed in the reactor and the mass of solid deposits on these sheets was measured after sufficient continuous running.

2.3. Process description

2.3.1. Conventional precipitation process

The conventional treatment process includes neutralization of the feed in a mix tank via injection of lime (or other base) at a controlled pH setpoint utilizing a PID controller (see Figure 1).

The product from the neutralization tank is fed to a clarifier for solid/liquid separation. The sludge is collected from the bottom of the clarifier and can either be pumped to a storage area or dewatered to increase its density prior to transport.

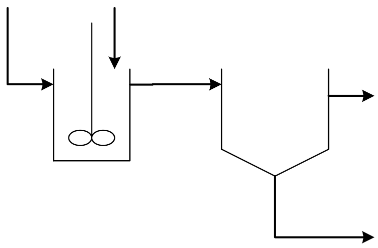


Figure 1. Conventional treatment.

2.3.2. Advanced precipitation processes

Advanced precipitation processes include sludge recirculation back to the neutralization tank to increase the solids concentration (see Figure 2).

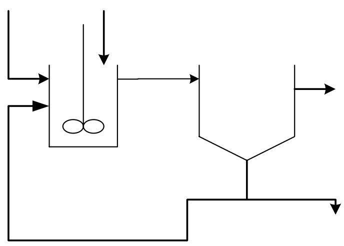


Figure 2. Advanced precipitation process.

2.4. Sludge Characterization

The characteristics of the crystals formed were analyzed to assess the objectives of this work. Through granulometry, it was possible to study the particle size distribution in the product slurry from the neutralization tank. The device used in the laboratory was a laser granulometer. It measures particle sizes in the range of 0,1 μm to 2mm.

Liquid–solid separation is another good, albeit relative indication of the precipitated solids characteristics. We compared the settling characteristics of the various product solids to gauge the impact of process and reactor configurations on the solid properties.

The thickening performance of sludges produced was evaluated using the Kynch-Modified, Talmage-Fitch method. This method provides a conservative thickener size based on a single settling curve in cases where the amount of slurry available for testing is low and/or rather consistent in terms of concentration, physical properties, etc. The free settling velocity of the particles obtained during the test can be used to asses the maximum hydraulic flux that a thickener could be expected to handle. Typically, the test is carried out in a 1–Liter graduate.

2.5. Reactor characterization

In many precipitation processes, the neutralization reactor operates at a high solids concentration (>10%w). Adequate mixing is needed to ensure a homogeneous mixture and minimize eddies and supersaturated zones inside the tank.

The relationship between the mechanism of suspension, tank geometry and scale-up parameters in stirred tanks are discussed in various papers but the results are far from conclusive (Chudacek, M.W., 1996; MontanteG, Pinelli D. et al., 2003. ; Jirickova E., Rieger F., 1995)

The density of the slurry inside the neutralization tank (and hence the solids concentration) was measured using a Coriolis mass flow device installed in a recirculating loop off the tank (see Figure 3).

For each experiment, we analyzed the slurry density versus impeller speed (rpm) from over a wide range of operation.

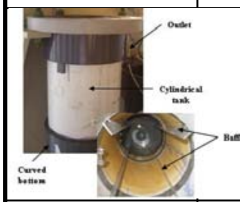
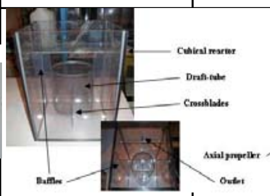
C.S.T.R (Continuous Stirred-Tank reactor)		**Turbomix**		**H.A.R.T.A.C.** (High-Aspect Ratio, Draft-Tube, Agitated Crystallizer)	
1.0L	*18.5L*	*1.5L*	*20L*	*1.25L*	*18.5L*
				confidential	confidential
ø$_{Impeller}$ - 46mm	ø$_{Impeller}$ - 116mm	ø$_{Impeller}$ - 46mm	ø$_{Impeller}$ - 116mm	confidential	confidential
Np = 1.2	Np = 0.8	Np = 1.2	Np = 0.8	confidential	confidential

Figure 3. Reactor and impeller characteristics.

3. RESULTS AND DISCUSSIONS

3.1. Scaling of gypsum

One reason why gypsum can be so problematic is that it accumulates on process equipment and piping slowly over time, causing operation and maintenance problems. Often times, the effluent portion of systems are susceptible to gypsum scale because the effluent is supersaturated with gypsum and precipitation continues outside of the controlled environment (Adams and Papangelakis, 2003). Scale formation is particularly troublesome in plants where lime is added directly to a wastewater containing a relatively high concentration of sulphate owing to the metastable nature of the effluent. Processes that include some form of solids recirculation back to the point of neutralization can reduce or eliminate the scaling because the increased particle surface area fosters secondary nucleation and reduces the level of gypsum supersaturation. In Figure 4, it is clear that sludge recirculation and the control of solids concentration in the neutralization tank can reduce post precipitation of gypsum and the associated solids deposition.

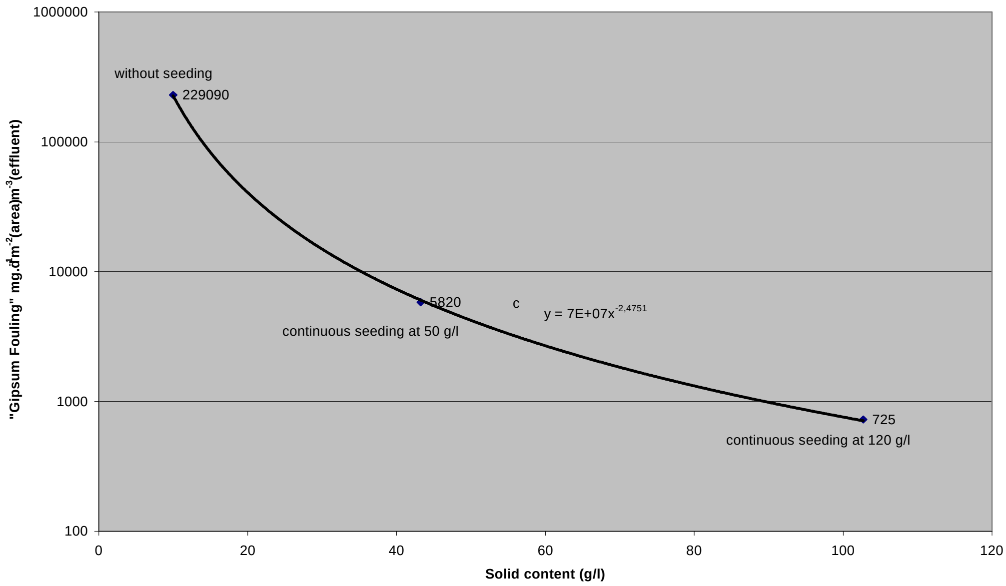


Figure 4. Gypsum scaling vs solid content.

3.2. Particle size distribution comparison

Figure 5 presents the PSDs obtained from each of the processes evaluated. The figure reveals superior performance of a process involving sludge recirculation versus a conventional process (as mentioned by Tapsell and Prijadi and Sunarho and Bickert and Amal, 2002).

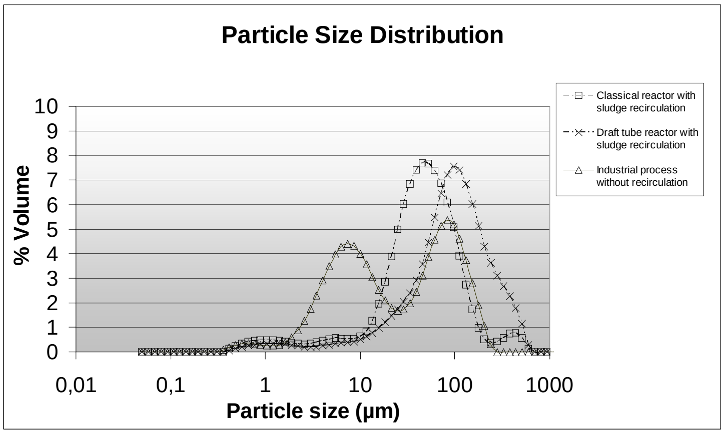


Figure 5. Sulfate System PSD – Impact of process and reactor design.

The various configurations tested emphasize the strong influence of agitation on the size quality of the formed crystals. For example, the mean particle size was increased about 20% by adjusting the agitator speed from high to low rpm (see Figure 6).

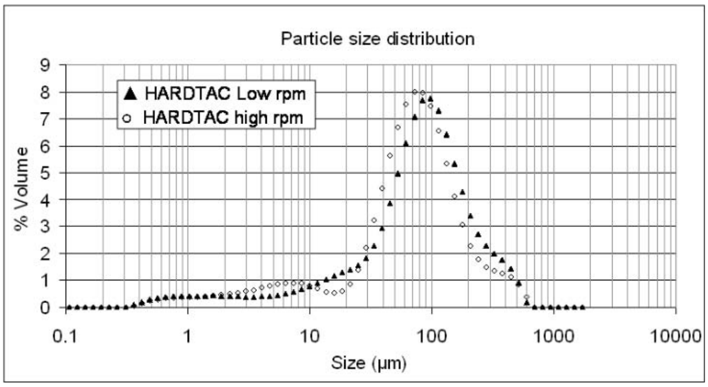


Figure 6. Sulphate System Particle Size Distributions – Impact of Mixing Speed.

For sulphate precipitation, the kinetics are very particular. A long induction time for low supersaturation means that the nucleation rate is very low. Sludge recirculation has the greatest effect on particle size and therefore, on solid–liquid separation.

3.3. Sludge dewatering comparison

Solid–liquid separation is quite dependant on particle size and distribution. Large solids with a relatively narrow PSD will be more easily separated by filtration than solids with a smaller size and/or a wider distribution. The effect of particle size on filtration rate and settling rate is approximately proportional to the square of the particle size, as given by Stoke's law:

$$v = \frac{gd^2(\rho_s - \rho_l)}{18\mu}$$

Where; v = terminal velocity
g = acceleration due to gravity
d = particle diameter
μ = viscosity of liquid
ρ_s, ρ_l = density of solid particle and of liquid

In practice, this means smaller equipment is needed to do the separation, and as such, reduces the capital investment of the equipment offsets the higher capital investment in the crystallizer. Therefore, it is very important to optimize the complete system. Process with sludge recirculation improve the sludge settling velocity and density (see Figure 8).

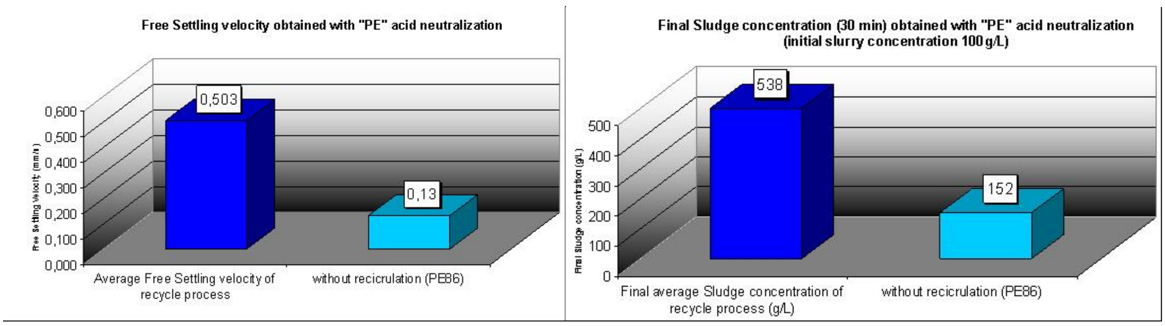


Figure 8. Settling properties.

3.4. Reactor characterization

In precipitation or crystallization processes, it is desirable to minimize supersaturated zones to control the nucleation rate. The nucleation rate is proportional to the square of the supersaturation concentration. A large sludge recirculation will result in smaller changes in supersaturation as the slurry circulates. An agitator with high pumping rates and large circulation flow insure good mixing and reduce local supersaturation. Additionally, a low attrition agitator promotes a well mixed solution without creating fine particles through attrition.

As the reactor is well mixed, the slurry concentration can be increased by increasing the total crystal surface area, reducing the supersaturation.

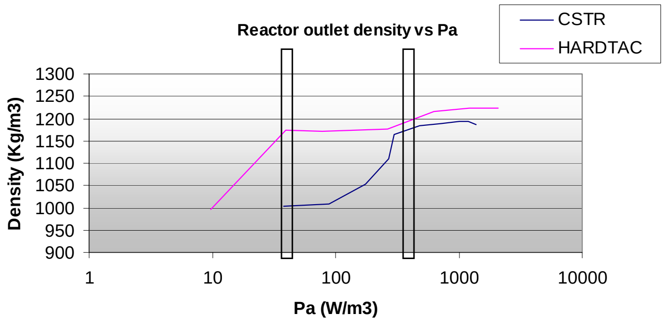


Figure 9. Minimum energy needed for homogenous suspension.

Draft tube reactor shows a better capability than classical one to have homogeneous solid suspension with lower energy reducing solid breakage

4. CONCLUSIONS

Recirculation of sludge reduces gypsum fouling and increases the particle size. Choosing an impeller with a high pumping rate and low shear provides an additional increase in particle size. This is due to minimizing primary nucleation and reducing attrition from shear.

While processes with sludge recirculation improve solid–liquid separation for sulphate removal systems, the variation of particle size between the different sludge recirculation processes does not appear to dramatically change the particle dewatering characteristics.

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