

Developments in Precipitation Engineering for the Process Intensification in the Environmental Protection and Other Purification Industrial Activities

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The realization of a precipitation process for the elimination of a harmful compound by the classical way needs a very large reactor volume due to low or very low concentrations of this compound. The paper shows some principal methods for the drastic decrease in precipitator volume based on the recycling and/or in situ separation of the solid phase. From simultaneous population and mass balances, some quantitative relations are obtained to estimate the reactor volume saving. The proposed methods can be used to realize low cost modifications of the existing plants in order to increase their capacity or to design new plants having reduced dimensions.

1. Introduction

In recent years, many methods are tested to be used in the treatment of wastes for the elimination of harmful compounds, but the methods based on precipitation remain generally the most important (and universal) for two principal reasons. First, the waste solutions have a very complex composition and are often very charged in different ions rendering the use of other methods (ion-exchange, membrane processes, electrodialysis, etc.) very uncertain. In these cases, only the precipitation processes are able to separate and recover with efficiency the harmful compounds from wastes before discharging. Second, even in the cases when other methods are preliminary used, the precipitation is practically always the last process transforming the harmful compounds to solid substances which can be stocked without danger and/or recycled.

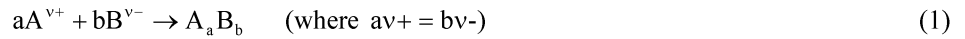
The precipitation is largely used and is practically irreplaceable process for the removing of heavy metals (Ayres et al., 1994) and/or other elements (calcium, magnesium, phosphorous, fluorine, etc.), as well as for the treatment of aqueous radioactive wastes (IAEA, 1992). The installations of the precipitation processes for the elimination from solutions of undesirable compounds are composed of a precipitator (generally a stirred tank) followed by a solid-liquid separation device (thickener or clarifier). Very often, the undesirable compound has a low or very low concentration, so the solid concentration in the reactor is very low. The rate of elimination of the undesirable compound by crystal growth depends on the surface area per cubic meter of the solid phase in the suspension. For this reason, the precipitation reactors have

generally a very large volume (for example, 5000 cubic meter reactors can be encountered in industry), which can sensibly increase the treatment cost of wastes. Recently, some studies (Chang, 1996; Meunier, 2006) compare the classical precipitation process with other separation processes (ion exchange, reverse osmosis, evaporation, electrochemical coagulation) for the wastewater pollution prevention and arrive to the conclusion that the last mentioned processes have a lower cost than the precipitation process. This conclusion is due to the fact that a classical precipitation process needs a very large reactor volume, so the decrease in the installation volume represents one of the principal ways to reduce the cost of the precipitation process and to make it more competitive than the others. In this context, the aim of the paper is to show the principal developments in the field of precipitation process engineering for the drastic decrease in the precipitator volume.

2. Classical precipitation process

Figure 1 shows the scheme of the classical precipitation process composed of a precipitator followed by a solid-liquid separation device. A is the harmful substance of initial concentration $C_{A,in}$ which is precipitated by the reagent B (concentration $C_{B,in}$) taken in stoichiometric excess according to the fixed outlet concentration $C_{A,out}$ of the substance A in the liquid phase. The outlet feed rate Q is equal to the sum of reagents feed rates $Q_A + Q_B$. In the clarifier, the feed rate Q is separated in two parts, the feed rate of the slurry q and the feed rate of the clear liquid phase $Q - q$. The quantity $n_{out}(L)$ is the population density of the solid phase at the outlet of the precipitator, while $n_f(L)$ is the final population density of the solid phase at the outlet of the installation.

The substance A precipitates according to the reaction:



From equation (1), the expression of the supersaturation can be obtained:

$$s = \gamma \left(C_{A,out}^a \cdot C_{B,out}^b \right)^{\frac{1}{a+b}} - P_s^{\frac{1}{a+b}} = \gamma \left\{ C_{A,out}^a \cdot \left[\frac{Q_B}{Q} C_{B,in} - \frac{b}{a} \left(\frac{Q_A}{Q} C_{A,in} - C_{A,out} \right) \right]^b \right\}^{\frac{1}{a+b}} - P_s^{\frac{1}{a+b}} \quad (2)$$

where γ is the activity coefficient and P_s – the solubility product. The concentrations $C_{A,in}$ and $C_{A,out}$ are given, so the supersaturation depends only on $C_{B,in}$.

The precipitator volume V is equal to $V=Q\tau$, where τ is the mean residence time of the suspension and Q – the feed rate at the outlet of the reactor. The mean residence time

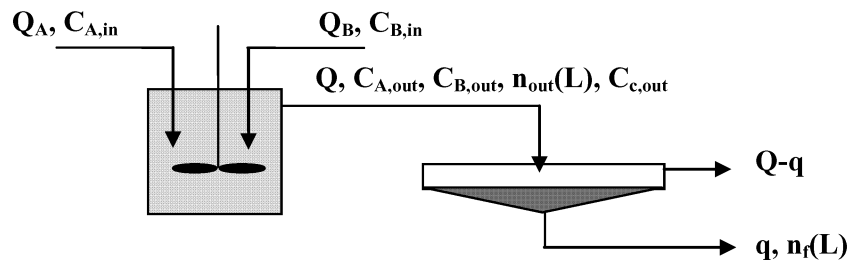


Fig. 1. Installation scheme of a classical precipitation process.

can be obtained from population and mass balances. In all this work, these balances are written assuming that the reactor is a perfectly stirred tank (MSMPR) functioning in steady state, the agglomeration and the breakage are negligible, the crystal growth rate G does not depend on the size of particles L and the size of nuclei is negligible in relation to the particles size. Under these hypotheses, the population balance of the fraction sizing from L to $L+dL$ is:

$$r_N V \delta(L) dL = d[GV n_{out}(L)] + Q n_{out}(L) dL \quad (3)$$

where r_N is the nucleation rate and $\delta(L)$ is the delta-function of Dirac. From balance equation (3) and knowing that all particles are produced in the reactor by nucleation, the following differential equation can be obtained:

$$G \frac{dn_{out}(L)}{dL} + \frac{n_{out}(L)}{\tau} = r_N \delta(L) \quad \text{with limiting condition} \quad \int_0^{\infty} n_{out}(L) dL = r_N \tau \quad (4)$$

$$\text{The solution of equation (4) is: } n_{out}(L) = \frac{r_N}{G} \cdot \exp\left(-\frac{L}{G\tau}\right) \quad (5)$$

The solid concentration of the suspension in and at the outlet of the reactor (in kg m^{-3}) can be calculated by the following expression:

$$C_{c,out} = \phi_v \rho_c \int_0^{\infty} L^3 n_{out}(L) dL = \phi_v \rho_c \frac{r_N}{G} \int_0^{\infty} L^3 \cdot \exp\left(-\frac{L}{G\tau}\right) dL = 6\phi_v \rho_c r_N G^3 \tau^4 \quad (6)$$

where ϕ_v is the volume shape factor and ρ_c – the density of particles. The nucleation and growth rates can be expressed by the following equations:

$$r_N = k_N C_c^m s^n \quad \text{and} \quad G = k_G s^g \quad (7)$$

Substituting equations (7) in equation (6), the expression for the calculation of the mean residence time can be obtained:

$$\tau = \left(\frac{C_{c,out}^{1-m}}{6\phi_v \rho_c k_N k_G^3 s^{n+3g}} \right)^{1/4} \quad (8)$$

The solid concentration C_c is derived from the following mass balance, where with M the molar masses of substances A and $A_a B_b$, are noted ($C_{A,in} \gg C_{A,out}$):

$$C_c = \alpha \left(\frac{Q_A}{Q} C_{A,in} - C_{A,out} \right) \approx \alpha \frac{Q_A}{Q} C_{A,in} \quad \text{where} \quad \alpha = \frac{M_{A_a B_b}}{a M_A} \quad (9)$$

Equations (2) and (8) show that the quantity of the precipitation reagent $Q_B C_{B,in}$ is the principal parameter for the calculation of the reactor volume. This quantity is determined by overall cost minimization taking into account the fact that the increase of $Q_B C_{B,in}$ reduces the volume of the reactor, and vice-versa.

3. Precipitation process with recycling

The scheme of a precipitation process with recycling and the principal quantities of population and mass balances are shown in Figure2. An important part of the sludge coming from the clarifier (thickener) is recycled with a feed rate q_R . The efficacy of installation depends on two pivot parameters, the recycling ratio $R = q_R/q$ and the liquid-

solid separation ratio $\lambda=Q/q$. Based on Figure 2, the population balance of the fraction sizing from L to $L+dL$ in the precipitator can be written as:

$$q_R n_f(L)dL + r_N V \delta(L)dL = d[GV n_{out}(L)] + (Q + q_R) n_{out}(L)dL \quad (10)$$

with limiting condition:

$$(Q + q_R) \int_0^\infty n_{out}(L)dL - q_R \int_0^\infty n_f(L)dL = r_N V \quad (11)$$

From the population balance of the clarifier, we have:

$$(Q + q_R) n_{out}(L)dL = (q + q_R) n_f(L)dL, \text{ so } n_f(L) = \frac{Q + q_R}{q + q_R} \cdot n_{out}(L) = \frac{\lambda + R}{1 + R} \cdot n_{out}(L) \quad (12)$$

The substitution of equation (12) in equations (10) and (11) gives:

$$G \frac{dn_{out}(L)}{dL} + \frac{\lambda + R}{\lambda(1 + R)} \cdot \frac{n_{out}(L)}{\tau} = r_N \delta(L) \text{ with } \frac{\lambda + R}{\lambda(1 + R)} \int_0^\infty n_{out}(L)dL = r_N \tau \quad (13)$$

The solution of this differential equation is:

$$n_{out}(L) = \frac{r_N}{G} \cdot \exp\left[-\frac{\lambda + R}{\lambda(1 + R)} \cdot \frac{L}{G\tau}\right] \quad (14)$$

and the solid concentration of the suspension in and at the outlet of the reactor (see equation 6):

$$C_{c,out} = \phi_v \rho_c \frac{r_N}{G} \int_0^\infty L^3 \cdot \exp\left(-\frac{\lambda + R}{\lambda(1 + R)} \cdot \frac{L}{G\tau}\right) dL = 6\phi_v \rho_c \left[\frac{\lambda(1 + R)}{\lambda + R}\right]^4 r_N G^3 \tau^4 \quad (15)$$

The substitution of the nucleation and crystal growth expressions in equation (15) gives:

$$\tau = \frac{\lambda + R}{\lambda(1 + R)} \cdot \left(\frac{C_{c,out}^{1-m}}{6\phi_v \rho_c k_N k_G^3 S^{n+3g}}\right)^{1/4} \quad (16)$$

The solid concentration $C_{c,out}$ can be determined from the mass balances of the reactor and the clarifier:

$$\begin{aligned} q_R C_{c,f} + \alpha[Q_A C_{A,in} - (Q + q_R) C_{A,out}] &= (Q + q_R) C_{c,out} \\ (Q + q_R) C_{c,out} &= (q + q_R) C_{c,f} \end{aligned} \quad (17)$$

From this system it follows ($C_{A,in} \gg C_{A,out}$):

$$C_{c,out} = \alpha \frac{1 + R}{\lambda + R} \left[\lambda \frac{Q_A}{Q} C_{A,in} - (\lambda + R) C_{A,out} \right] \approx \alpha \frac{\lambda(1 + R)}{\lambda + R} \cdot \frac{Q_A}{Q} C_{A,in} \quad (18)$$

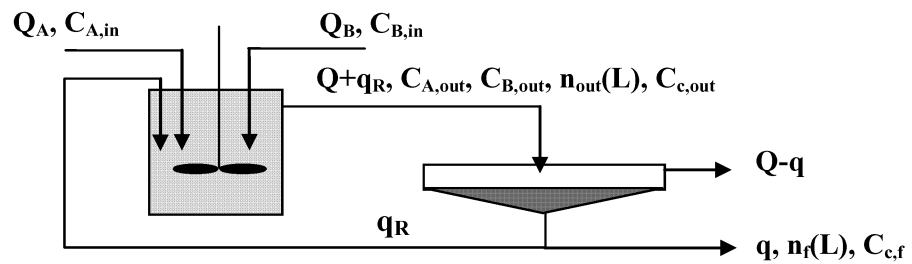


Fig. 2. Installation scheme of the precipitation process with recycling.

Equations (8) and (9), as well as equations (16) and (18) are used to compare the reactor volumes of the classical process V_{class} and of the process with recycling V_{recyc} for the same supersaturation value (the same $C_{B,\text{in}}$ and $C_{A,\text{out}}$):

$$\frac{V_{\text{recyc}}}{V_{\text{class}}} = \frac{\tau_{\text{recyc}}}{\tau_{\text{class}}} = \left[\frac{\lambda + R}{\lambda(1 + R)} \right]^{\frac{3+m}{4}} \quad (19)$$

Equation (19) shows that the reactor volume can be sensibly reduced if the recycling of an important sludge quantity is used. The exponent "m" is of the order of 0 for the primary nucleation mechanism, but it can vary from 1 to 2 in the case of the secondary nucleation mechanism with a predominant value around 1. For a rapid estimation of the reactor volume reduction we recommend to use $m = 1$. In addition, we can remark that the liquid-solid separation factor is very high (for example, about 20), so for $m = 1$, equation (19) can be simplified ($\lambda \rightarrow \infty$) to equation (20) showing in a more obvious manner the influence of the recycling ratio on the diminution of the precipitator volume:

$$\frac{V_{\text{recyc}}}{V_{\text{class}}} = \frac{\tau_{\text{recyc}}}{\tau_{\text{class}}} \approx \frac{1}{1 + R} \quad (20)$$

4. Other more efficient precipitation processes and discussion

Recently, a new reactor composed of a perfectly mixed precipitation zone of volume V_{pz} and a clarifier (see Fig.3) is applied for the precipitation of struvite (Mangin et al., 2006). Using the population balance of the reactor, we can easily prove (the demonstration is not shown here) that this kind of installation corresponds to the special case with recycling having a recycling ratio equal to infinity, so from equation (19):

$$\frac{V_{\text{pz}}}{V_{\text{class}}} = \frac{\tau_{\text{pz}}}{\tau_{\text{class}}} = \left(\frac{1}{\lambda} \right)^{\frac{3+m}{4}} \approx \frac{1}{\lambda} \quad (21)$$

Equation (21) proves that the volume of the precipitation process can be drastically reduced when this kind of installation is used. Nevertheless, the perfectly mixed zone has a low precipitation rate due to the low supersaturation corresponding to the outlet very low limit concentration of the undesirable compound. This inconvenience is avoided in a fluidized bed column with or without stirring (Fig.3), where the fluid flow approaches the plug flow, so the precipitation zone of the fluidized bed installation has a smaller volume than this one of the installation with a perfectly stirred tank. The volume calculation of the precipitation zone of the fluidized bed installation is very complex and is out of the scope of this paper. Nevertheless, equation (21) can be used in practice for a rough rapid estimation of the reduction of the precipitation volume when the fluidized bed substitutes a classical precipitation reactor.

Agglomeration is an important phenomenon during the elimination of impurities by precipitation and in many cases flocculants are added to accelerate the process. The agglomeration (flocculation) increases enormously the size of the particles decreasing drastically the sedimentation surface and the total volume of the liquid-solid separator. Mathematical developments of this paper did not take into account this phenomenon. Generally, two kinds of agglomerates can be encountered: "loose" and compact. In the

first case, the agglomerates are totally open, so any elementary particle keeps the contact with the liquid phase and can independently grow as it would be free. In this case, the above mathematical expressions can be applied. In the second case (compact agglomerates), only the external surface of the agglomerates participates in growth, so the effect of volume decrease is less pronounced than this one predicted by the above equations (the volume calculation is much more complex and is not shown here). Nevertheless, the rate of agglomeration is proportional to the square of particles concentration, thus the last mentioned processes produce bigger size particles needing smaller size clarifiers to be separated. Generally speaking, the recycling, the perfectly mixed tank with classification and, especially, the fluidized bed precipitator (mentioned according to increased efficiency), can sensibly decrease the volume of the precipitation zone as well as the volume of the liquid-solid separator giving a purification installation much smaller than the installation using the classical process.

The methods described here can be successfully used for the designing of new installations and/or for improving the functioning and increasing the capacity of existing installations. Especially, the use of sludge recycling is recommended in the case of existing installations, because very low cost modifications can sensibly increase their capacity. When a new installation has to be constructed, we recommend the use of the fluidized bed, which represents the most efficient device for process intensification in the environmental protection or other purification industrial activities.

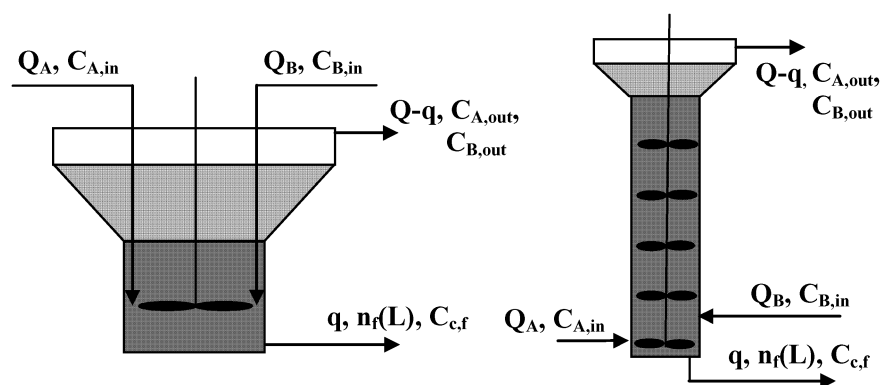


Fig. 3. Installation schemes of the precipitation processes with solid classification (left) and with a fluidized bed reactor (right).

5. References

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