# Chapter 4
# Precipitation of Heavy Metals

**Alison Lewis**

**Abstract** Precipitation is the process of solid formation from solution by means of a reaction. It is most frequently used in the removal and recovery of metals from solution. In scientific terms, precipitation is affected by a chemical reaction that forms a salt whose solubility in solution is exceeded. The thermodynamic driving force causing precipitation is called supersaturation. Definitions of supersaturation are not consistent in the literature, and a variety of equations are used for the calculation of supersaturation. The major mechanisms comprising precipitation are nucleation, growth and agglomeration. High supersaturation levels favour nucleation, whilst lower levels favour crystal growth. Agglomeration occurs in the presence of large numbers of particles, in a supersaturated environment.

Precipitation is commonly used for metal removal from wastewaters, but is not yet commonly used for metal recovery from wastewaters. Metal hydroxide precipitation is the most commonly used method, although metal sulphide precipitation has many advantages. Other methods of metal removal can be in the form of sulphate (e.g. $CaSO_4.2H_2O$) or fluoride (e.g. $CaF$) salts.

Crystalliser design for water treatment ranges in complexity from the simplest pipe reactor to the more sophisticated fluidised bed reactor, which is an extremely effective design for metal removal and recovery.

In summary, when using precipitation as an extremely effective metal removal and recovery method, careful attention must be paid to designing precipitation systems that are able to produce precipitates with desirable separation characteristics.

**Keywords** Precipitation • Supersaturation • Solubility • Nucleation • Growth • Agglomeration • Metal hydroxide • Metal sulphide • Fluidised bed reactor

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# 4.1   Introduction

Precipitation is defined as the process that occurs when, by virtue of a chemical reaction, the solubility of a salt in solution is exceeded. In this case, the solution is said to be supersaturated with respect to the precipitating compound, meaning the solute concentration is higher than the solid-liquid equilibrium value. The degree of supersaturation is important because it is the driving force for the precipitation process and is always required to effect precipitation.

In the case of precipitation, the method used to alter the equilibrium conditions and thus to generate supersaturation is the addition of another substance or reagent to the system (Ullmann and Gerhartz 1998).

For example, the mixing of two reagents, such as $CuSO_4$ and $Na_2S$, results in the following chemical reaction.

$$CuSO_4 + Na_2S \rightarrow CuS(s) + Na_2SO_4 \qquad (4.1)$$
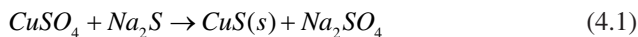
The chemical reaction creates the sparingly soluble salt, CuS, which, because its solubility is exceeded, will precipitate out of solution.

### 4.1.1   Thermodynamics of Precipitation

In more technical terms, if a system is to be in thermodynamic equilibrium, then the requirement is that there must be equal chemical potentials of each component through all phases. Let $\mu_{Liquid}$ and $\mu_{Solid}$ (J/mol) be the chemical potential of the precipitating salt in the solution and as a solid, respectively. If the system is in equilibrium then:

$$\mu_{Liquid,eq} = \mu_{Solid} \tag{4.2}$$

Suppose the system is driven out of its equilibrium state due to some external action, e.g. addition of another substance, so that the solution becomes supersaturated. The chemical potential of the solute in solution $\mu_{Liquid}$ is now higher than the corresponding equilibrium value $\mu_{Liquid,eq}$. The difference between the chemical potential of the solute in the supersaturated and the saturated state is represented by $\Delta\mu$ (J/mol), and is the thermodynamic driving force for precipitation:

$$\Delta\mu = \mu_{Liquid} - \mu_{Liquid,eq} = \mu_{Liquid} - \mu_{Solid} \tag{4.3}$$

This thermodynamic driving force is referred to as the supersaturation.

In the case of precipitation with the solid composed of more than one solute of a chemical formula of the type: $A_{vA}B_{vB}\ldots I_{vi}$, i.e. formed by $\nu_i$ units of species $i$, the equation for the driving force is written:

$$\Delta\mu = RT\ \ln\frac{\Pi a_i^{v_i}}{K_{sp}} = \frac{\Pi\left(\gamma_i c_i\right)^{v_i}}{K_{sp}} = RT\ \ln S_{am} \tag{4.4}$$

$$K_{sp} = \Pi\left(\gamma_{i,eq} c_{i,eq}\right)^{v_i} \tag{4.5}$$

Where

$R$ = ideal gas constant [J/mol/K]
$T$ = temperature *[K]*
$a$ = activity of the solute [M]
$\nu_i$ = number of the i$^{th}$ ion in a molecule of the crystal
$\gamma_i$ = activity coefficients of the solute in solution [−]
$c$ = molar concentration of the solute in solution
$K_{sp}$ = solubility product of the solid [m$^v$]
$S_{am}$ = activity-based supersaturation ratio for multiple solutes [−]

Following on from this the supersaturation, $S_{am}$, is written as:

$$S_{am} = \frac{\Pi\left(\gamma_i c_i\right)^{v_i}}{K_{sp}} \tag{4.6}$$

There is some discrepancy in the expressions for supersaturation that exist in the literature. For example, Sohnel and Garside (1992) give the following equation:

$$S_a = \frac{a_{\pm}}{a_{\pm,eq}} \tag{4.7}$$

Where

$S_a$ = dimensionless supersaturation based on activities
$a_{\pm}$ = mean activity
$a_{\pm,eq}$ = mean activity at equilibrium (i.e. the solubility product)

Whereas Kashchiev and van Rosmalen (2003) give the following, for ionic molecules which dissociate into solution as ions of type i = 1, 2, …, j:

$$s_a = \left(\frac{a_1^{v1} a_2^{v2} \ldots a_j^{vj}}{a_{1,eq}^{v1} a_{2,eq}^{v2} \ldots a_{j,eq}^{vj}}\right)^{\frac{1}{(v_1 + v_2 + \ldots + v_j)}} \tag{4.8}$$

Where

$v_i$ = number of the ith ion in a molecule of the crystal;
$a_i$ = actual activities of these ions in the solution ($m^{-3}$).
$a_{i,e}$ = equilibrium activities of these ions in the solution ($m^{-3}$), i.e. the solubility product

For molecules such as $BaSO_4$ and $CaCO_3$, where $v_1 = v_2 = 1$, i.e. there is one cation and one anion in a molecule of a crystal, this equation simplifies to:

$$s_a = \left(\frac{a_1^1 a_2^2}{K_{sp}}\right)^{\frac{1}{2}} \tag{4.9}$$

Thus, when dealing with the calculation of the supersaturation, it is important to always check on the definition being used, as these are not consistent in the literature.

**Nucleation:**
birth of particles

**Growth:**
Enlargement of
particles by material
deposition

**Agglomeration:**
Enlargement of particles
due to the growth of
crystaline bridges between
them
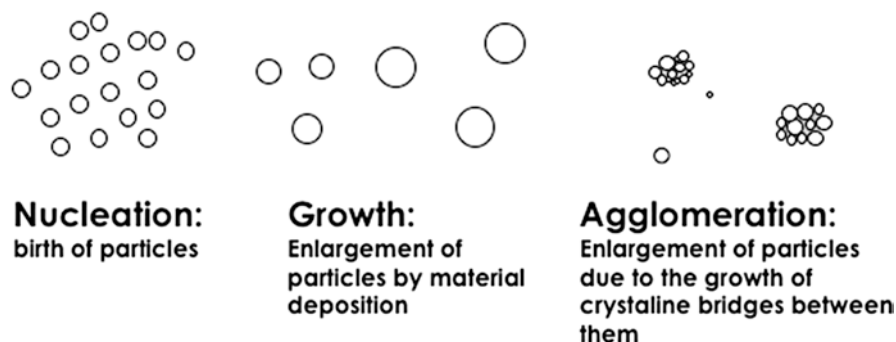
**Fig. 4.1** Summary of the three major precipitation mechanisms: nucleation, growth and agglomeration

## 4.1.2    Kinetics of Precipitation

Once it has been established that a precipitation process is thermodynamically possible, in other words, that the solution is supersaturated with respect to the precipitating phase, it is usually of interest to establish the kinetics of the process, i.e. how fast the process is likely to happen. This involves understanding the various mechanisms by which the precipitation process occurs. The mechanisms are summarised in Fig. 4.1.

- **Nucleation**

Nucleation is the initial formation of the solid phase from solution. It occurs once the clusters and aggregates of molecules or ions in a supersaturated solution achieve a critical size, i.e. one at which the entities will grow rather than redissolve (Jones et al. 2004). Primary homogenous nucleation is the birth of a solid phase spontaneously from solution, whereas primary heterogeneous nucleation is induced by the presence of foreign particles. Secondary nucleation is induced by the presence of existing crystals and can take many forms, including contact nucleation such as crystal-crystal contact or crystal-crystalliser contact, shear nucleation such as that due to fluid flow, fracture nucleation due to particle impact, attrition nucleation due to particle impact from fluid flow and needle nucleation due to particle disruption (Jones et al. 2004).

The rate of nucleation is a function of supersaturation, with very high supersaturation levels favouring primary nucleation, and slightly lower levels favouring secondary nucleation.

- **Growth**

Growth is the process whereby crystals become enlarged due to the deposition of crystalline material on an existing crystal surface.

The growth rate is also a function of the supersaturation, with growth occurring at lower levels of supersaturation than that required for nucleation. The type of
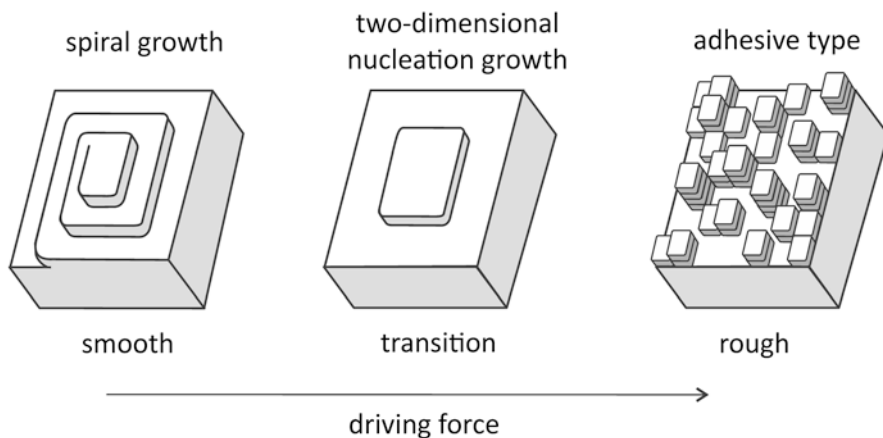
**Fig. 4.2**  Relationship between supersaturation and type of growth (Lewis et al. 2015)

growth that will occur is also influenced by the supersaturation levels, with rough growth favoured at high supersaturation levels, birth and spread growth favoured at intermediate supersaturation levels, and spiral or smooth growth favoured at low supersaturation levels. See Fig. 4.2.

It is the relative rates at which nucleation and growth occur that determine the final particle size distribution. As would be expected, when the rate of nucleation is high relative to the growth rate, the crystals formed are small and highly numerous (Kroschwitz and Seidel 2006). This is frequently the case in precipitation from solution in water treatment processes.

- **Agglomeration**

Agglomeration is the process in which two or more particles are brought in contact and stay together for a sufficiently long period such that a crystalline bridge between the particles can grow. Thus a stable particle or agglomerate is formed.

As for nucleation and growth, the rate of agglomeration is a function of the supersaturation but also, since it is a collision-driven process, a function of the square of the numbers of particles present. Therefore, it follows that, when there is a high degree of nucleation in a process, which leads to the formation of high numbers of particles, the collision rate, and thus the agglomeration rate, is likely to be high.

Sometimes particle agglomeration is the only available method of size enlargement in a precipitation process. Because of the large numbers of particles involved, it usually plays an important, but not always desirable, role in the formation of larger particles in precipitation and crystallisation processes (Lewis et al. 2015). As would be expected, agglomerates usually have a lower degree of purity than crystals that become larger due to crystal growth, as mother liquor tends to become trapped in the interstitial spaces between the agglomerated crystals.
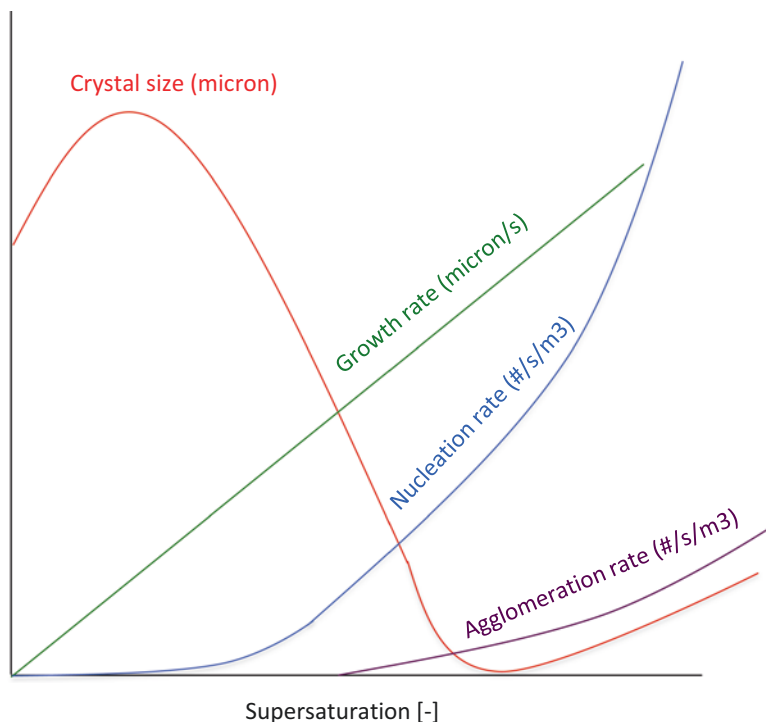
**Fig. 4.3** Relationship between supersaturation, nucleation, growth and agglomeration as well as crystal size. With an increase in supersaturation, the growth rate increases linearly. After a critical supersaturation, the nucleation rate increases exponentially. Agglomeration becomes significant at higher supersaturation levels (Lewis et al. 2015)

Figure 4.3 summarises the relationships between the supersaturation, the crystal size and the three main precipitation mechanisms outlined above.

## 4.2 Use of Precipitation in Removal and Recovery of Metals from Wastewater

Precipitation is commonly used for metal removal from various types of wastewaters, including hydrometallurgical effluents and acid mine drainage. Once the metals have been precipitated, they can be filtered, centrifuged, or separated by another means from the remaining aqueous phase. In addition, if a voluminous precipitate is formed, it can effectively "sweep" ions and particles from the wastewater (USEPA 2000).

Although chemical precipitation is used in around 90 % of treatment plants treating industrial wastewaters (Schiewer and Volesky 2000; Grijalva 2009), recovery of metals by precipitation is not yet common practice. Currently, the primary objective is the removal of the metals for the purpose of water treatment, and not for the metal values themselves.

**Table 4.1** Solubility constants of metals for four different metal salts

|          | Solubility products (Log $K_{sp}$) | | | |
|----------|--------|----------|------------|--------|
| Metal    | $OH^-$ | $CO_3^{2-}$ | $PO_4^{3-}$ | $S^{2-}$ |
| $Ag^+$   | −7.7   | −11.1    | −17.6      | −49    |
| $Cd^{2+}$ | −14.3 | −13.7    | −32.6      | −28.9  |
| $Co^{2+}$ | −15.9 | −12.8    | –          | –      |
| $Cu^+$   | −19.4  | −9.6     | −35.1      | −36    |
| $Fe^{2+}$ | −15.9 | −10.6    | −36        | −16.8  |
| $Fe^{3+}$ | −37.1 | –        | –          | –      |
| $Hg^{2+}$ | −25.4 | −22.5    | –          | −52    |
| $Ni^{2+}$ | −17.2 | −6.8     | −31.3      | −18.5  |
| $Pb^{2+}$ | –     | −13.1    | −44.5      | −28.1  |
| $Zn^{2+}$ | −15.6 | −10.3    | −36.7      | −22    |

The United States Environmental Protection Agency (USEPA) initiated some of the early patents on metal removal by chemical precipitation in order to treat wastewater (Wemhoff 1984; Greenberg 1990). There are a number of possible chemical precipitation methods for removing heavy metals[1] from wastewater, including hydroxide ($OH^-$), sulphide ($S^{2-}$), carbonate ($CO_3^{2-}$) and phosphate ($PO_4^{3-}$) precipitation. The solubilities of these most commonly employed metal salts is given in Table 4.1 (Grijalva 2009).

Other precipitation methods for wastewater treatment employ calcium hydroxide for the removal of fluoride from industrial wastewater as calcium fluoride (Aldaco et al. 2005).

## 4.3   Metal Hydroxide Precipitation

### 4.3.1   Advantages

Metal hydroxide precipitation is the most widely used of the chemical precipitation techniques for water treatment, mostly because it is cheap, easy to implement and can be relatively easily controlled by controlling pH. Traditionally, water treatment processes, especially water neutralisation processes, have been based on chemical neutralisation using a base such as quicklime (CaO), hydrated lime ($Ca(OH)_2$, limestone ($CaCO_3$) or the hydroxides of Mg, Na and $NH_4^+$. When a solution containing dissolved metal ions is contacted with a base, the result is precipitation of the metals in solution as metal hydroxides.

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[1] There is no widely agreed criteria-based definition of a heavy metal. See Duffus, J. H. (2002). "Heavy metals" a meaningless term? (IUPAC Technical Report)." Pure and Applied Chemistry **74**(5): 793–807. http://dx.doi.org/10.1351/pac200274050793
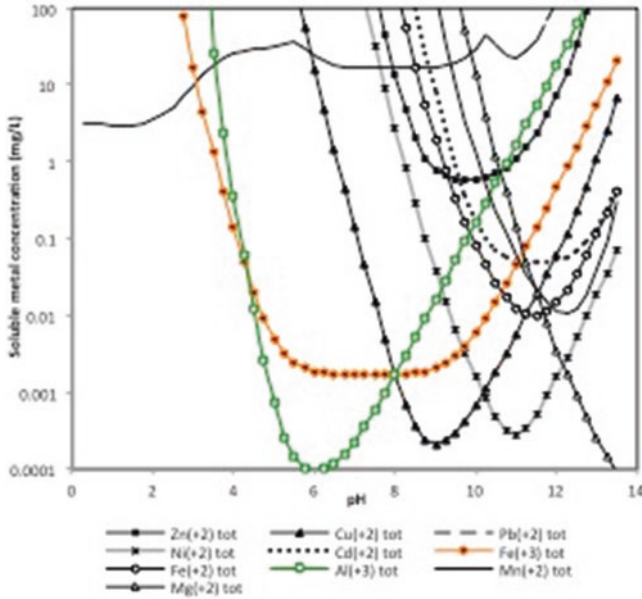
**Fig. 4.4** Metal hydroxide solubilities as a function of pH (Lewis 2010)

## *4.3.2  Disadvantages*

Although this method is the most widely used, it has several disadvantages, namely high cost, lack of effectiveness in reducing sulphate in solution and the formation of large volumes of sludge, which require disposal (Erdem and Tumen 2004).

In addition, the final metal concentration level that can be achieved is not very low and concentrations remain at levels from 0.5 to 2 mg/L (Grijalva 2009). See Fig. 4.4, which shows that the minimum dissolved concentration that can be achieved by hydroxide precipitation is ±0.0005 ppm at pH levels between 6 and 12. An additional difficulty is that hydroxides tend to form gelatinous precipitates that are difficult to thicken or filter (Peters 1985).

## 4.4  Metal Sulphide Precipitation

## *4.4.1  Previous Studies*

Although several studies have been conducted on precipitation of metal sulphides from solution (Bryson and Bijsterveld 1991; Mishra and Das 1992; Rickard 1995; Harmandas and Koutsoukos 1996; Veeken et al. 2003; van Hille et al. 2004, 2005;

Bijmans et al. 2009; Sampaio et al. 2010), the physico-chemical processes of nucle-
ation and crystal growth involved in the precipitation of metals as sulphides still
remain uncertain.

The review article by Lewis (2010) pointed out how the study of metal sulphide
precipitation has been extremely fragmented, with the research being carried out in
the disparate areas of: (1) fundamental studies, which have usually focused on
mechanisms and have been carried out at very low (micromolar) concentrations, (2)
applied studies, which have usually focused on metal removal and aqueous phase
reaction kinetics, (3) solid phase studies, which have focused on the crystallisation
kinetics of the formed solids; (4) precipitation studies, which have focused on pre-
cipitation of metal sulphide nanocrystals. The last area of focus has been (5) metal
sulphide precipitation in effluent treatment such as acid mine drainage and indus-
trial hydrometallurgical processes.

## 4.4.2   Advantages

Metal sulphide precipitation is another method of removing metal ions for wastewa-
ter treatment. This method has the advantage of the potentially high removal effi-
ciency and selective metal precipitation over a broad pH range.

One of the main advantages of sulphide precipitation can be seen in Fig. 4.5,
which shows the metal sulphide solubilities as a function of pH. Figures 4.5 shows
that the solubilities of a range of metal sulphides is extremely low. This means that
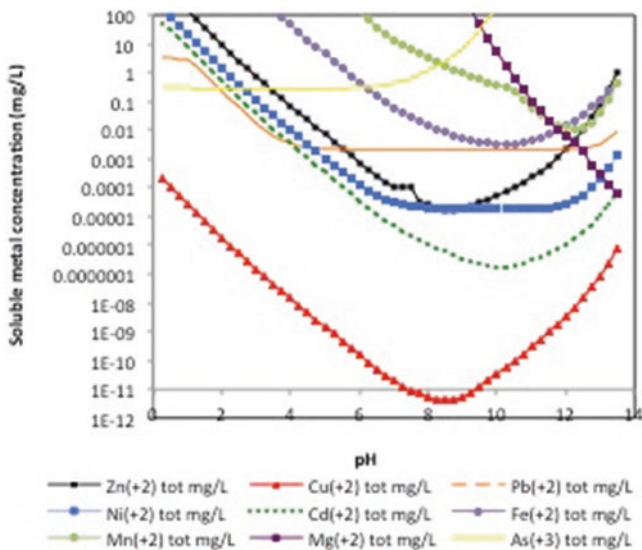there is potential for effective metal removal to extremely low concentrations.



**Fig. 4.5** Metal sulphide solubilities as a function of pH (Lewis 2010)

For example, the minimum residual Cd concentration when Cd is removed as a metal sulphide is less than 0.0001 mg/L, which occurs at any pH greater than 6 (see Fig. 4.5, compared to the minimum residual Cd concentration of 0.048 mg/L when Cd is removed as a hydroxide at pH 11.5 (See Fig. 4.4).

In chemical process applications, this treatment technology has been relatively limited due to the cost of the chemicals, but also due to safety concerns around the generation of hydrogen sulphide gas, particularly when treating acidic effluents (Nduna and Lewis 2014).

However, metal sulphide precipitation has more recently been successfully used as a means to remove metals from solution in the treatment of acid mine drainage, also called acid rock drainage. Here, sulphate-reducing bacteria are used, during which process the acidic sulphate is reduced to sulphide by the bacteria. Tabak et al. (2003) developed a resource recovery-based remediation process to clean up a polluted mine site in the USA. Veeken and Rulkens (2003) investigated selective precipitation of heavy metals using a sulphide-selective electrode for control. Kaksonen and Puhakka (2007) carried out a review of various passive and active SRB-based alternatives as well as some process design aspects, such as reactor types, process configurations, and choices of substrates for sulphate reduction. Huisman et al. (2006) described a biological process that produced sulphide $H_2S$ from elemental sulphur, waste sulphuric acid or sulphate present in effluents. This $H_2S$ was then used in an engineered, high rate bioreactor to treat metal containing effluents.

Aside from the safety concerns mentioned above, the use of $H_2S$ as a gaseous form of sulphide has many advantages, including the fact that the produced metal sulphides have good settleability and filterability (Huisman et al. 2006). The mechanism by which the $H_2S$ improves the particle properties is due to the fact that the gaseous sulphide source decreases the rate of generation of supersaturation by exploiting the mass-transfer resistance to dissolution of $H_2S(g)$ and thus exerts a measure of control over the precipitation process (Karbanee et al. 2008).

### 4.4.3 Disadvantages and Challenges

The essential problem with being able to use metal sulphide effectively for metal removal and recovery remains the particle characteristics of the formed metal sulphide precipitates. Because of the extremely low solubilities of the metal sulphide salts, this means that the process will be driven by very high supersaturations. As a consequence of this extremely high driving force, the resulting precipitation reaction is difficult to control and a large number of submicron particles are formed during the process. Thus, solid-liquid separation and subsequent recovery become a significant technical challenge and, despite the low solubility and theoretically high efficiency of metal sulphide precipitation processes, the practical efficiency is often significantly lower.

**Fig. 4.6** Relationship
between the pH of
precipitation and the zeta
potential of the precipitated
particles for CuS and ZnS
(Lewis and Nduna 2014)
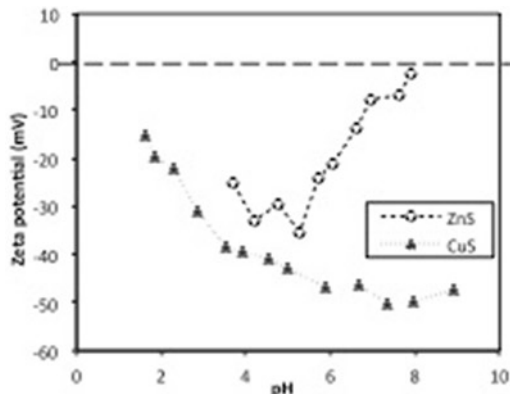


In addition, colloidal metal sulphide precipitates exhibit surface properties that often prevent agglomeration and therefore settling of the precipitates. This has been demonstrated in a number of works that examined the effect of the pH at which the metal sulphide particles were precipitated and their resulting zeta potential (Mokone et al. 2010; Nduna et al. 2013). The findings show that there is a strong relationship between the measured zeta potential of the final particles and the precipitation pH. As can be seen in Fig. 4.6, for CuS, there is a marked decrease in zeta potential, i.e. the zeta potential becomes more negative, as the precipitation pH increases from 2 to 9. In contrast, for ZnS, the zeta potential increases, i.e. becomes less negative, as the precipitation pH is increased from 6 to 8. This is due to the effects of two counteracting phenomena. As the pH increases, the effect of the increasing concentration of $S^{2-}$ ions is felt, and the zeta potential decreases. At the same time, the metal cations exert a counteracting positive effect.

Other works have focused on how the metal to sulphide molar ratio affects the final precipitated particles (Mokone et al. 2010, 2012a, b). It was found that, in the CuS system, a large number of small copper sulphide particles, with highly negatively charged surfaces and poor settling characteristics, were formed in the presence of a stoichiometric excess of sulphide at pH 6. In contrast, for ZnS, the metal to sulphide molar ratio did not have a significant effect on the number and size of the particles formed. This emphasises that the concentration of reactive sulphide species in solution is crucial in determining the nature and surface characteristics of the particles produced.

A number of methods can be used to mitigate the effect of the very high supersaturation conditions experienced in metal sulphide precipitation, including recycling a portion of the precipitated settled solids to the reaction vessel (Adams et al. 2008), adding the reagent, usually $H_2S$, to a mixture of feed solution and recycled solids (Merritt et al. 1985) or redesigning the reactor itself to minimise locally high supersaturation levels (Lewis et al. 2015).

### *4.4.4 Post Precipitation Conditions*

It is also known that downstream processing conditions have an effect on the surface properties of the colloidal particles produced during metal sulphide precipitation. This downstream processing can include the addition of divalent and trivalent cations such as ($Ca^{2+}$) and ($Al^{3+}$) that can favourably modify the precipitate properties. Mokone et al. (2012a, b) showed that, where supersaturation cannot be managed, downstream processing that changes the surface properties of colloidal metal sulphide precipitates can lead to effective solid-liquid separation.

## 4.5   Sulphate Salts

It is also possible to remove and recover sulphur as sulphate salts, without the reduction step. An example of this is the removal of sulphate via precipitation of gypsum ($CaSO_4.2H_2O$) from acid mine drainage and lime (Dill et al. 1998). In this case, calcium hydroxide is provided as the source of calcium and, in the case of acid mine drainage, the added calcium ions react with sulphate ions, and produce a gypsum precipitate, among other mineral compounds. As in the case of metal sulphide precipitation, it has been found that gypsum forms very small particles during precipitation, which are difficult to separate from the treated liquid through gravitational settling or filtration. According to Bowell (2004), the low solubility of $CaSO_4.2H_2O$ results in a low residual $SO_4^{2-}$ level of about 0.24 g/100 ml at 20 °C, after $CaSO_4.2H_2O$ removal. However, metals are not removed via this method, except via adsorption onto the precipitated gypsum.

## 4.6   Crystalliser Design for Wastewater Treatment

In order to successfully remove metals from wastewater using precipitation, the design of a crystalliser or reactor that can deliver the necessary particle characteristics is crucial. The default industrial practice is the stirred tank reactor, with reagents being added at a single point and mixed into the reactor bulk using a central impeller. This method leads to very poor particle characteristics, whether sulphide or hydroxide precipitates.

### *4.6.1 Pipe Reactor*

An extremely simple metal sulphide precipitation reactor that is frequently used in industry is the "pipe reactor". This simple pipe junction design, schematically illustrated in Fig. 4.7, exploits the very rapid kinetics of the metal sulphide precipitation
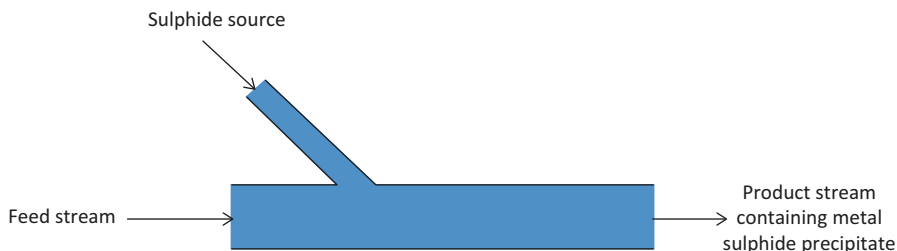
**Fig. 4.7** Schematic of the pipe reactor commonly used in industry

reaction, which occurs in the pipe itself. The advantages of this reactor are the simplicity and ease of operation. The disadvantages are that the local supersaturation induced by introducing the sulphide in this manner is extremely high, and thus the particle properties are usually poor.

### 4.6.2 Fluidised Bed Reactor

One of the most successful methods that has been employed for wastewater treatment via precipitation is the use of the Fluidised Bed Reactor.

#### 4.6.2.1 Crystalliser Description

Fluidised Bed Reactors have been identified as an effective reactor configuration for processes in which the product is a sparingly soluble species that is difficult to separate. Fluidised Bed Reactors have been extensively used in industry with applications in the softening of potable water (Aldaco et al. 2007) and in the removal of heavy metals, phosphates and fluorides from wastewater (Seckler 1994). Aqueous waste streams generated from acid mine drainage, electroplating and base metal refining operations, with dissolved metal concentrations varying from 10 to 100,000 ppm have also been successfully treated using precipitation in fluidised bed reactors (Wilms et al. 1992; Zhou et al. 1999; Guillard and Lewis 2001, 2002; Kaksonen et al. 2003; van Hille et al. 2005; Costodes and Lewis 2006).

Fluidised bed reactors provide ideal conditions for controlled precipitation and as a result present many advantages over conventional chemical precipitation processes. Some of the advantages of fluidised bed reactors are:

- Fluidisation allows for good mixing on both the macro and meso-scale, so that local supersaturation levels can be controlled.
- Supersaturation can be controlled through multiple reagent inlet ports.
- The product can be separated from the treated water using gravitational separation, as the large crystals migrate to the bottom of the bed where they are

harvested (Al-Othman and Demopoulos 2009). Fines generated during precipitation can be recycled and allowed to agglomerate, thus forming large particles, which can be recovered, thus increasing the solid-liquid separation efficiency (Heffels and Kind 1999; Guillard and Lewis 2001). Fluidised bed reactors are typically modelled as plug flow reactors (Levenspiel 1999, 2002)

- Physical phenomena are accurately described by the axial dispersion model (Toyokura et al. 1973; Wojcik 1999).
- Crystal-impeller collisions, like those in a stirred tank reactor, which result in attrition, and therefore fines generation, are eliminated.

In a fluidised bed reactor, the vessel is charged with a batch of pre-characterised seeds, which are subsequently fluidised by the aqueous metal stream entering the reactor from the bottom. The reagent is fed through inlet ports situated on the side of the reactor. Figure 4.8 illustrates the working principle of the reactor.

As precipitate is deposited on the seeding material, the particle size distribution along the height of the column changes. Larger, denser particles migrate to the bottom of the reactor where they are removed as a product, while the lighter particles remain suspended higher up in the bed. In continuous processes, new seeding material is introduced at the top of the reactor, while large particles are removed at
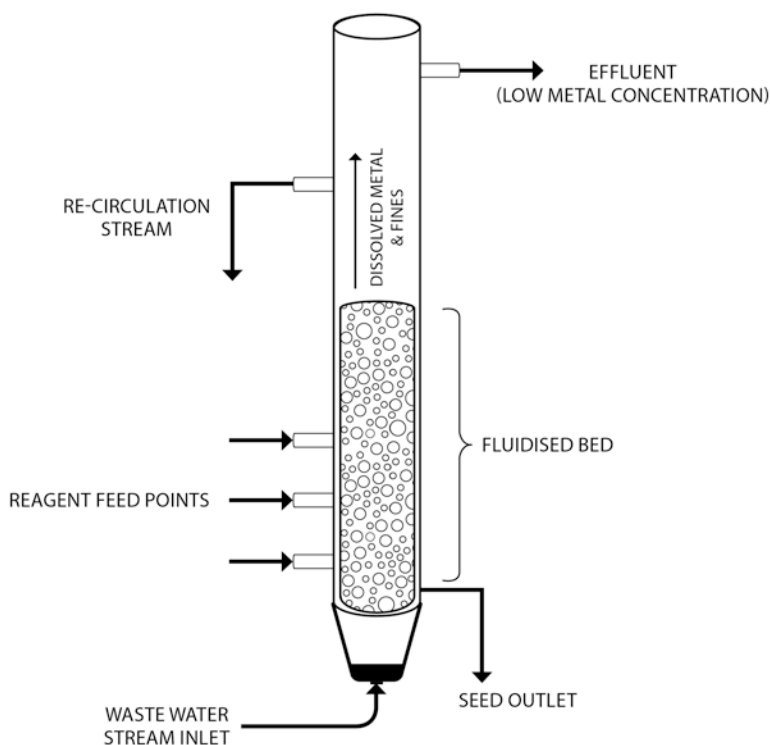


**Fig. 4.8** Schematic of a fluidised bed crystalliser (Adapted from Seckler 1994)

the bottom to maintain a constant bed height (Guillard and Lewis 2001; van Hille et al. 2005). The remaining mother liquor exits the top of the reactor. In some cases, the effluent stream is recirculated to increase conversion of unreacted metal. Key parameters of operation are the reactant feed rates, recirculation rate, the initial height of the bed at zero flow and size and type of seeds.

### 4.6.2.2   Seeding

The fluidised bed reactor operates on the principle of seeded precipitation, i.e. the supersaturated solution is seeded with small particles of the crystallising material in order to promote particle growth onto the seeds and to prevent homogenous nucleation in the bulk solution. The choice of seed material intended for use in a fluidised bed reactor is such that bubbling or channelling inside the bed as well as high pressure drops across the bed are avoided (Rhodes 2008). Guillard and Lewis (2001) successfully crystallised nickel carbonate on silica seeds; van Hille et al. (2005) crystallised copper sulphide on silica seeds, and Seckler (1994) crystallised calcium phosphate onto silica seeds. A study by Tai et al. (1999) found that the use of silica requires an induction time for crystal growth. This is due to the activation energy of crystal growth on seeds of a different crystal being higher than for seeds of the same material.

The specific surface area of the seeding material has an influence on the efficiency of the entire process since precipitation mechanisms such as nucleation, growth and agglomeration are all surface dependant (Wang and Anderson 1992). These mechanisms are therefore sensitive to the nature of the surface, the specific surface area, as well as the number of active sites available (Randolph and Larson 1988).

The specific surface area provided by the seeding material is initially very large, but declines as seeds increase in size and are subsequently removed from the reactor. The specific active surface area of seeds needs to remain sufficiently large to promote crystal growth. Hence, coated seeds should remain relatively small, that is diameters less than 1 mm (Seckler 1994). It is also important to ensure that seed sizes remain small since larger crystals tend to generate more secondary nuclei in agitated systems than smaller crystals (Mullin 2001).

### 4.6.2.3   Supersaturation in a Fluidised Bed Reactor

It is very difficult to obtain a uniform supersaturation in any reactor and high local supersaturation zones lead to spontaneous primary nucleation The supersaturation profile within a fluidised bed reactor forms a gradient with a high degree of supersaturation closer to reagent inlet ports towards the lower region of the reactor, and decreases along the height of the reactor as a result of the progressing precipitation reaction.

In an attempt to control supersaturation, feeding the base reagent through multiple inlet ports along the side of the reactor has been found to be effective (Seckler 1994; Guillard and Lewis 2001; van Hille et al. 2005). Other techniques include stepwise addition of the precipitating agent and solvent dilution (Al-Othman and Demopoulos 2009). Stepwise addition of the alkaline solution allows the slow release of reaction components. This was shown to grow large crystals and is successfully applied to acid neutralisation precipitation processes (Tai 1999; Karidakis et al. 2005; Gómez 2013). Solvent dilution on the other hand, allows for a lower concentration of the alkaline solution and better control over reaction components (Mullin 2001).

Seckler (1994) showed inconsistent supersaturation levels within a fluidised bed crystalliser, with the general trend observed of decreasing levels of supersaturation along the height of the bed, while the highest levels are around the reactor inlet points (Guillard and Lewis 2001).

### 4.6.2.4  Product Quality and Efficiency

The desired product quality of the precipitated compounds is that they are easily separable from the residual solution for reuse. The presence of fines makes separation and recovery difficult. In fluidised bed reactors, elutriation of fines out of the bed by the effluent is the primary factor contributing to inefficiencies (Seckler 1994; Guillard and Lewis 2001; van Hille et al. 2005). The formation of fines is usually avoided by using seeded precipitation, however in the presence of high supersaturation zones at the reactant inlet ports or due to channelling, particularly in the fluidised bed, fines may still form through primary nucleation. Furthermore, high-energy dissipation zones (predominantly at the bottom of the reactor and inlet ports) trigger fines formation through attrition when crystals collide. However, maintaining a small average seed size minimises fines formation through this mechanism.

In practice, metal removal via precipitation in fluidised bed reactors yields good results. Seckler (1994) achieved metal recoveries of between 80 % and 95 % in phosphate precipitation, while Guillard et al. (2002) achieved removal efficiencies exceeding 90 % in nickel carbonate precipitation using fluidised bed reactors. Metal concentrations from 10 up to 100,000 ppm can be treated (Van Ammers et al. 1986).

## 4.7  Conclusion

Precipitation has the potential to be an effective method of removing metals from solution to very low concentrations. It has the drawback of producing particles that can be difficult to separate. Appropriate reactor design, such as the fluidised bed reactor, is one of the possible methods to mitigate this. In addition, most of the studies focus on removal, not recovery, of metals from solution. This is an area that needs to be addressed in the future (Table 4.1).

# References

Adams M, Lawrence R, Bratty M (2008) Biogenic sulphide for cyanide recycle and copper recovery in gold-copper ore processing. Miner Eng 21(6):509–517. http://dx.doi.org/10.1016/j.mineng.2008.02.001

Aldaco R, Irabien A, Luis P (2005) Fluidized bed reactor for fluoride removal. Chem Eng J 107(1–3):113–117. http://dx.doi.org/10.1016/j.cej.2004.12.017

Aldaco R, Garea A, Irabien A (2007) Particle growth kinetics of calcium fluoride in a fluidized bed reactor. Chem Eng Sci 62(11):2958–2966. http://dx.doi.org/10.1016/j.ces.2007.02.045

Al-Othman A, Demopoulos GR (2009) Gypsum crystallization and hydrochloric acid regeneration by reaction of calcium chloride solution with sulfuric acid. Hydrometallurgy 96(1–2):95–102. http://dx.doi.org/10.1016/j.hydromet.2008.08.010

Bijmans MFM, van Helvoort P-J, Buisman CJN, Lens PNL (2009) Effect of the sulphide concentration on zinc bio-precipitation in a single stage sulfidogenic bioreactor at pH 5.5. Sep Purif Technol 69(3):243–248. http://dx.doi.org/10.1016/j.seppur.2009.07.023

Bryson AW, Bijsterveld CH (1991) Kinetics of the precipitation of manganese and cobalt sulphides in the purification of a manganese sulphate electrolyte. Hydrometallurgy 27(1):75–84. http://dx.doi.org/10.1016/0304-386x(91)90079-2

Costodes VCT, Lewis AE (2006) Reactive crystallization of nickel hydroxy-carbonate in fluidized-bed reactor: fines production and column design. Chem Eng Sci 61(5):1377–1385. http://dx.doi.org/10.1016/j.ces.2005.08.038

Dill S, Cowan J, Wood A Bowell R (1998) A review of sulfate removal options for mine waters. International Mine Water Association Proceedings. Johannesburg, South Africa, pp 329–342

Duffus JH (2002) Heavy metals a meaningless term? (IUPAC Technical Report). Pure Appl Chem 74(5):793–807. http://dx.doi.org/10.1351/pac200274050793

Erdem M, Tumen F (2004) Chromium removal from aqueous solution by the ferrite process. J Hazard Mater 109(1):71–77

Gómez DKV (2013) Simultaneous sulfate reduction and metal precipitation in an inverse fluidized bed reactor. PhD thesis, UNESCO-IHE Institute for Water Education, Delft, the Netherlands

Greenberg B (1990) Precipitation of heavy metal oxides; controlling water pollution, Google Patents

Grijalva VMG (2009) Biological and physical-chemical methods for treatment of semiconductor manufacturing effluents. Doctor of Philosophy, University of Arizona, USA

Guillard D, Lewis AE (2001) Nickel carbonate precipitation in a fluidized-bed reactor. Ind Eng Chem Res 40(23):5564–5569. http://dx.doi.org/10.1021/ie010312q

Guillard D, Lewis AE (2002) Optimization of nickel hydroxycarbonate precipitation using a laboratory pellet reactor. Ind Eng Chem Res 41(13):3110–3114. http://dx.doi.org/10.1021/ie010873h

Harmandas NG, Koutsoukos PG (1996) The formation of iron(II) sulfides in aqueous solutions. J Cryst Growth 167(3–4):719–724. http://dx.doi.org/10.1016/0022-0248(96)00257-6

Heffels S, Kind M (1999) Seeding technology: an underestimated critical success factor for crystallization. In: Proceedings of the 14th International Symposium on Industrial Crystallization, Institution of Chemical Engineers, Warwickshire, UK

Huisman JL, Schouten G, Schultz C (2006) Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy 83(1–4):106–113. http://dx.doi.org/10.1016/j.hydromet.2006.03.017

Jones A, Rigopoulos S, Zauner R (2004) Crystallization and precipitation engineering. In: Barbosa-Póvoa A, Matos H (eds) Computer aided chemical engineering, vol 18. Elsevier, Amsterdam, pp 75–86. http://dx.doi.org/10.1016/S1570-7946(04)80084-1

Kaksonen AH, Puhakka JA (2007) Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals. Eng Life Sci 7(6):541–564. http://dx.doi.org/10.1002/elsc.200720216

Kaksonen AH, Riekkola-Vanhanen ML, Puhakka JA (2003) Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater. Water Res 37(2):255–266. http://dx.doi.org/10.1016/s0043-1354(02)00267-1

Karbanee N, Van Hille RP, Lewis AE (2008) Controlled nickel sulphide precipitation using gaseous hydrogen sulphide. Ind Eng Chem Res 47(5):1596–1602. http://dx.doi.org/10.1021/ie0711224

Karidakis T, Agatzini-Leonardou S, Neou-Syngouna P (2005) Removal of magnesium from nickel laterite leach liquors by chemical precipitation using calcium hydroxide and the potential use of the precipitate as a filler material. Hydrometallurgy 76(1):105–114. http://dx.doi.org/10.1016/j.hydromet.2004.09.007

Kashchiev D, van Rosmalen GM (2003) Review: nucleation in solutions revisited. Cryst Res Technol 38(7–8):555–574. http://dx.doi.org/10.1002/crat.200310070

Kroschwitz JI, Seidel A (2006) Kirk-Othmer encyclopedia of chemical technology, Wiley. http://dx.doi.org/10.1002/crat.200310070

Levenspiel O (1999) Chemical reaction engineering. Ind Eng Chem Res 38(11):4140–4143. doi:10.1021/ie990488g

Levenspiel O (2002) Modeling in chemical engineering. Chem Eng Sci 57(22):4691–4696. https://doi.org/10.1016/S0009-2509(02)00280-4

Lewis AE (2010) Review of metal sulphide precipitation. Hydrometallurgy 104(2):222–234. http://dx.doi.org/10.1016/j.hydromet.2010.06.010

Lewis AE, Nduna M (2014) Improving surface charge and particle size in precipitation of métal sulphides. 19th International Symposium on Industrial Crystallization (ISIC19), Toulouse, France, 16–19 September,

Lewis AE, Seckler MM, Kramer H, van Rosmalen GM (2015) Industrial crystallization: fundamentals and applications. Cambridge University Press. http://dx.doi.org/10.1017/cbo9781107280427

Merritt RC, Seidel DC, Burnham DA, Bush PD (1985) Recovery from solution. In: Weiss NL (ed) SME mineral processing handbook, vol 2. Society of Mining Engineers of the Americal Institute of Mining, Metallurgical, and Petroleum Engineers, New York, pp 51–59

Mishra PK, Das RP (1992) Kinetics of zinc and cobalt sulphide precipitation and its application in hydrometallurgical separation. Hydrometallurgy 28(3):373–379. http://dx.doi.org/10.1016/0304-386x(92)90042-x

Mokone TP, van Hille RP, Lewis AE (2010) Effect of solution chemistry on particle characteristics during metal sulphide precipitation. J Colloid Interface Sci 351(1):10–18. http://dx.doi.org/10.1016/j.jcis.2010.06.027

Mokone TP, Lewis AE, van Hille RP (2012a) Effect of post-precipitation conditions on surface properties of colloidal metal sulphide precipitates. Hydrometallurgy 119–120:55–66. http://dx.doi.org/10.1016/j.hydromet.2012.02.015

Mokone TP, van Hille RP, Lewis AE (2012b) Metal sulphides from wastewater: assessing the impact of supersaturation control strategies. Water Res 46(7):2088–2100. http://dx.doi.org/10.1016/j.watres.2012.01.027

Mullin JW (2001) Crystallization. Butterworth-Heinemann. http://dx.doi.org/10.1021/op0101005

Nduna M, Lewis A (2014) Removal of metal ions from industrial effluents and acid mine drainage by metal sulphide precipitation. Water Research Commission, Research Project No. K5/2108

Nduna M, Rodriguez-Pascual M, Lewis A (2013) Effect of dissolved precipitating ions on the settling characteristics of copper sulphide. J South Afr Inst Min Metall 113(5):00–00. Available from: <http://www.scielo.org.za/scielo.php?script=sci_arttext&pid=S0038-223X2013000500009&lng=en&nrm=iso>. ISSN 2411-9717

Peters RW (1985) Evaluation of recent treatment techniques for removal of heavy metals from industrial wastewaters. American Industrial Chemical Engineering Symposium Series, Citeseer

Randolph AD, Larson MA (1988) Theory of particulate processes: analysis and techniques of continuous crystallization. Academic, New York. http://dx.doi.org/10.1002/aic.690180343

Rhodes MJ (2008) Introduction to particle technology. Wiley, Weinheim. http://dx.doi.org/10.1002/9780470727102

Rickard D (1995) Kinetics of FeS precipitation: part 1. Competing reaction mechanisms. Geochim Cosmochim Acta 59(21):4367–4379. http://dx.doi.org/10.1016/0016-7037(95)00251-t

Sampaio R, Timmers R, Kocks N, André V, Duarte M, van Hullebusch E, Farges F, Lens P (2010) Zn-Ni sulfide selective precipitation: the role of supersaturation. Sep Purif Technol 74(1):108–118. http://dx.doi.org/10.1016/j.seppur.2010.05.013

Schiewer S, Volesky B (2000) In: Lovley DR (ed) Biosorption processes for heavy metal removal. Environmental microbe-metal interactions. ASM Press, Washington, pp 329–362. http://dx.doi.org/10.1128/9781555818098.ch14

Seckler MM (1994) Calcium phosphate precipitation in a fluidized bed. PhD Thesis, Delft University of Technology, Delft, The Netherlands

Söhnel O, Garside J (1992) Precipitation – basic principles and industrial application. Butterworth Heinemann Ltd, Oxford

Tabak HH, Scharp R, Burckle J, Kawahara FK, Govind R (2003) Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. Biodegradation 14(6):423–436. http://dx.doi.org/10.1023/a:1027332902740

Tai CY (1999) Crystal growth kinetics of two-step growth process in liquid fluidized-bed crystallizers. J Cryst Growth 206(1–2):109–118. http://dx.doi.org/10.1016/s0022-0248(99)00300-0

Tai CY, Chien WC, Chen CY (1999) Crystal growth kinetics of calcite in a dense fluidized-bed crystallizer. AICHE J 45(8):1605–1614. http://dx.doi.org/10.1002/aic.690450802

Toyokura K, Tanaka H, Tanahashi J (1973) Size distribution of crystals from classified bed type crystallizer. J Chem Eng Japan 6(4):325–331. http://dx.doi.org/10.1252/jcej.6.325

Ullmann F Gerhartz W (1998) Ullmann's encyclopedia of industrial chemistry, VCH. http://dx.doi.org/10.1002/14356007

USEPA (2000) Wastewater technology fact sheet. Chemical Precipitation. US EPA Washington, DC

Van Ammers M, Van Dijk J, Graveland A, Nühn P (1986) State of the art of pellet softening in the Netherlands. Water Supply 4:223–235

van Hille R, Foster T, Storey A, Duncan J Lewis A (2004) Heavy metal precipitation by sulphide and bicarbonate: evaluating methods to predict anaerobic digester overflow performance. In: International Mine Water Association Symposium 2004: Mine Water 2004 – Process, Policy, and Progress, Newcastle upon Tyne, United kingdom

van Hille RP, Peterson KA, Lewis AE (2005) Copper sulphide precipitation in a fluidised bed reactor. Chem Eng Sci 60(10):2571–2578. http://dx.doi.org/10.1016/j.ces.2004.11.052

Veeken A, de Vries S, van der Mark A, Rulkens W (2003) Selective precipitation of heavy metals as controlled by a sulphide-selective electrode. Sep Sci Technol 38:1–19. http://dx.doi.org/10.1081/ss-120016695

Wang Y, Anderson P (1992) Effect of the surface characteristics of seed on copper precipitation. Water Sci Technol 26(9–11):2141–2143

Wemhoff MF (1984) Recovery of metal from waste water by chemical precipitation, Google Patents

Wilms D, Vercaemst K, Van Dijk J (1992) Recovery of silver by crystallization of silver carbonate in a fluidized-bed reactor. Water Res 26(2):235–239. https://doi.org/10.1016/0043-1354(92)90223-Q

Wojcik JA (1999) Modelling of fluidized-bed crystallizers. 14th International Symposium on Industrial Crystallization, Institute of Chemical Engineers (IChemE), United Kingdom

Zhou P, Huang J-C, Li AWF, Wei S (1999) Heavy metal removal from wastewater in fluidized bed reactor. Water Res 33(8):1918–1924. http://dx.doi.org/10.1016/s0043-1354(98)00376-5