

GYPSUM SCALE FORMATION IN HYDROMETALLURGICAL OPERATIONS AND FLOTATION

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ABSTRACT. The presence of gypsum scale formations on the technological equipment surfaces is a common problem in industrial technological processes. The scale formations contaminate equipment surfaces, reducing the processes' effectiveness and cause higher maintenance costs. The paper presents the results of a study on the scale formation in machinery and equipment, used in hydrometallurgical operations and flotation, as well as technological possibilities for their elimination.

Key words: scale formations, hydrometallurgical operations, flotation

ОБРАЗУВАНЕ НА ГИПСОВИ ОТЛАГАНИЯ ПРИ ХИДРОМЕТАЛУРГИЧНИ ОПЕРАЦИИ И ФЛОТАЦИЯ НА РУДИ

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РЕЗЮМЕ. Наличието на гипсови отлагания върху повърхности на технологично оборудване е често срещан проблем при промишлени технологични процеси. Гипсовите отлагания замърсяват повърхностите на оборудването, намаляват ефективността на процесите и са причина за повишаване разходите за поддръжка. В доклада е представено извършеното проучване на формирането на гипсови отлагания в машини и съоръжения, използвани при хидрометалургични операции и флотация на руди, както и технологични възможности за елиминирането им.

Ключови думи: гипсови отлагания, хидрометалургични операции, флотация на руди

Introduction

Scale formation or deposition of inorganic salts from aqueous solutions onto surfaces is a widespread problem in many industrial processes. These formations can be hard, crystalline and strongly adherent deposits, or soft porous, loosely held sludge (Hasson, 1981). Scale formation is an issue because it fouls equipment surfaces, reducing process efficiency and increasing maintenance costs. Industries and processes where scale formation is most common include oil and gas production, geothermal energy production, desalination operations, steam generation, heat transfer systems, water supply systems as well as hydrometallurgical and flotation operations.

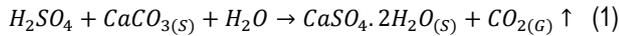
The main objective of the paper is to review the gypsum scale formation in machinery and equipment, used in hydrometallurgical and flotation operations, as well as to identify possible technological approaches for the elimination of these formations.

Gypsum scale formation in hydrometallurgical operations

In hydrometallurgical operations, a wide variety of scale formations are commonly encountered. High temperatures and high ionic strengths make their formation unavoidable. One example is the formation of hematite and alunite scales on autoclave walls during high temperature leaching of nickeliferous laterites. (Perdikis, 1996). Another example from the field of hydrometallurgy is the formation of calcium sulfate scales, mostly dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), but also semihydrates ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and anhydrite (CaSO_4), depending on the temperature and operating conditions.

Due to the very low solubility of the calcium sulfate hydrates, the scales are deposited almost anywhere where calcium and sulfate are present in aqueous solutions. The result is fouled reactor walls, impellers and pumps, as well as clogged pipes. Gypsum scales are formed even at low pH and can only be removed mechanically (Nulty, 1991)

The largest occurrence of gypsum scale formations in hydrometallurgical operations is during the partial or total neutralization of acidic leach solutions with limestone (CaCO_3) and lime (CaO). The reactions are:



Since the reactors operate at atmospheric pressure and temperature below 90°C , gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the primary reaction product. Under these conditions, gypsum is the precipitating phase. (Hand, 1997; Ostroff, 1964; Posnjak, 1938).

In the treatment of nickeliferous laterite ore both partial and total neutralization stages are required. A simplified process flowsheet of the process is given in Figure 1.

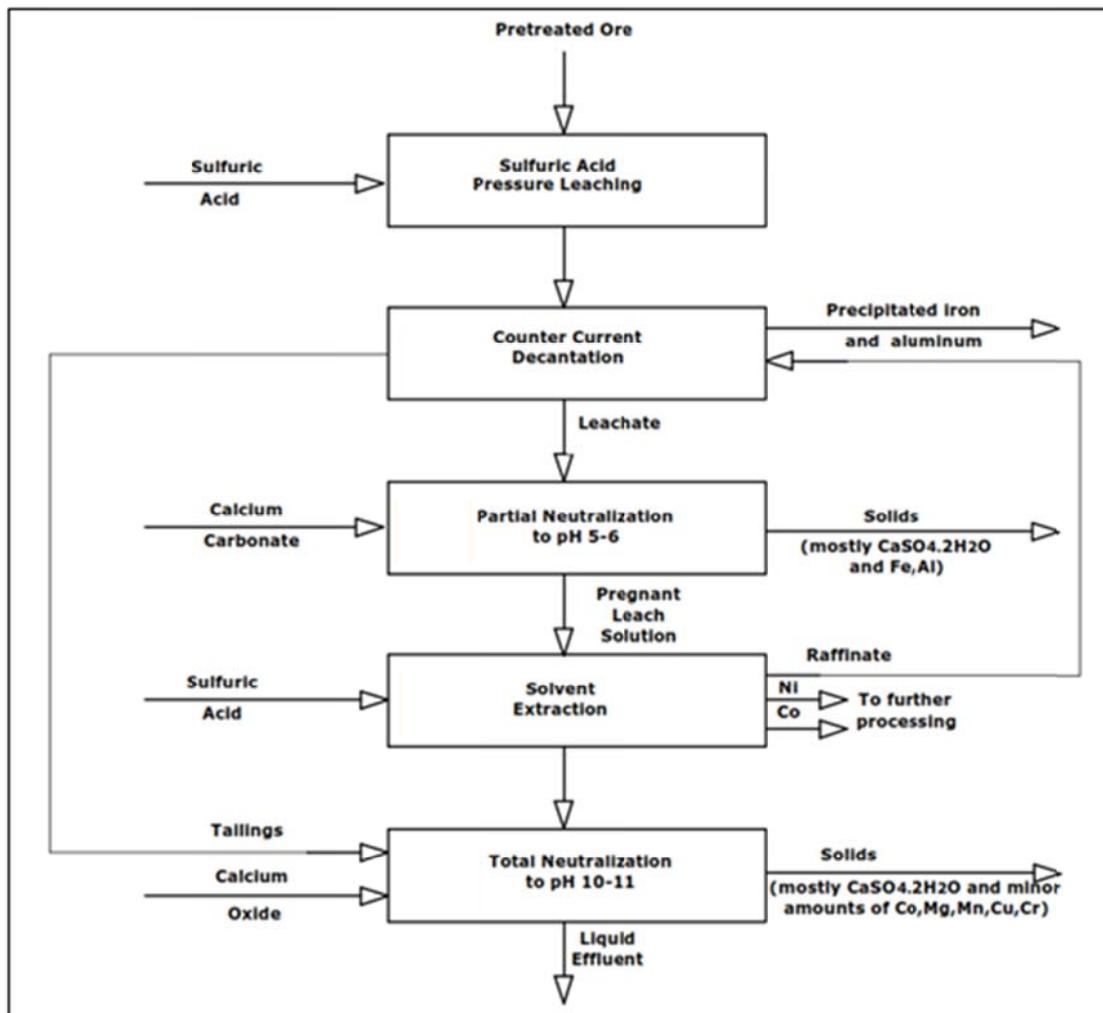


Fig. 1. Simplified process flowsheet of nickeliferous laterite ore treatment

The neutralization (reaction 1) takes place right after the high-temperature laterite leaching. The autoclave effluent is in the form of slurry and contains precipitated iron and aluminium, as well as dissolved iron, aluminium, nickel, minor amounts of cobalt, magnesium, manganese, chromium, copper, some trace impurities and free sulfuric acid. The leach slurry temperature and pressure are first reduced and then it is subjected to the counter current decantation (CCD) stage (Perdikis, 1996). Further, the liquid phase leaving the CCD is partially neutralized to a pH of 5-6 with limestone (reaction 1) to precipitate the remaining in solution iron, aluminium and sulfate, and to adjust the pH for subsequent nickel/cobalt treatment steps.

From the partial neutralization step, the resulting slurry is again separated and the pregnant leach solution continues to a solvent extraction operation, while the residue containing solid gypsum, iron, and aluminium is sent to waste impoundment.

The recovered leach solution, containing target nickel and cobalt metals is directed to the solvent extraction stage. The metals are extracted using an appropriate solvent extractant followed by stripping with sulfuric acid and further processing for nickel and cobalt recovery. The solvent extraction raffinate is sent to a final total neutralization stage (reaction 2) to neutralize the sulfuric acid and to precipitate out all of the remaining metal ions.

The issue of gypsum scale formation occurs in both neutralization stages. It leads not only to gypsum precipitation in the bulk solution, but also to scale deposition on reactor surfaces and in pipes around the reactors.

Gypsum scale formation in flotation

In the flotation of polymetallic sulfide minerals, especially complex sulfide ores the pyrite can only be depressed at very high additions of lime. The best pH range for pyrite depression is between 10 and 12. The high pH and oxidizing atmosphere leads to formation of calcium hydroxide and calcium sulfate at the pyrite surface. At high pH formation of iron (III) hydroxide also occurs. These hydrophilic species account for the complete depression of pyrite by lime treatment. The activation flotation of the lime depressed pyrite is to remove these hydrophilic coatings. Sulfuric acid is the main activator for the flotation of depressed pyrite, however it causes environmental and scale formations problems due to the large additions of sulfuric acid required.

Figure 2 shows the addition points of slaked lime and sulfuric acid in DPM Chelopech flotation plant and Figure 3 – gypsum scale formations in the DPM Chelopech flotation plant equipment.

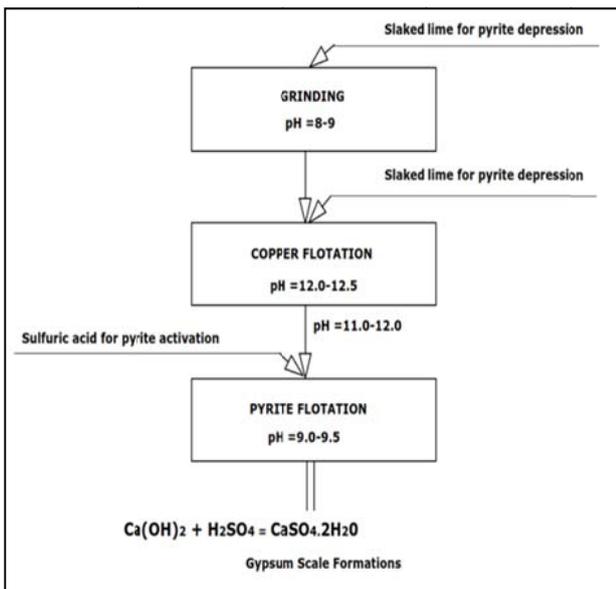


Fig. 2. Addition points of slaked lime and sulfuric acid in DPM Chelopech flotation plant



Fig. 3. Gypsum scale formations in the DPM Chelopech flotation plant equipment

Gypsum scale formation mechanism

In order to understand the mechanism of gypsum scales formation, it is necessary to review the fundamental crystal theory, which includes crystal precipitation, nucleation, and growth theory.

Crystal precipitation

Precipitation is defined "as reactive crystallization, i.e. the production of a solid compound out of a solution via a chemical reaction"(Dirksen, 1991).

Nucleation

If the saturation ratio S is above 1, the first stage of crystal formation commences. This stage is called nucleation and it has three main categories: (1) primary homogeneous, (2) primary heterogeneous and (3) secondary heterogeneous.

Primary homogeneous nucleation occurs in bulk solution, in the absence of a solid interface (Dirksen, 1991). This is done through solute molecules combining to form nuclei. These nuclei either reach a critical size above which they are stable, or dissolve back into solution. Homogeneous nucleation occurs at relatively high values of S , because the interfacial energy between the crystal and the solution is relatively high, and therefore a substantial driving force is necessary for it to occur (Stumm, 1992)

Primary heterogeneous nucleation occurs in the presence of an external surface. Nuclei form on a solid surface such as grime, reactor or pipe walls, colloidal particles, etc. In this case, the interfacial energy between the crystal and the solid is less than the interfacial energy between the crystal and solution. Thus, primary heterogeneous nucleation occurs at lower values of S than primary homogeneous nucleation. (Dirksen, 1991; Stumm, 1992).

Secondary heterogeneous nucleation occurs on seed particles of the same composition and phase as the precipitating ones. When these seed particles are purposefully added to the solution to induce precipitation, it is called apparent secondary nucleation. When the seed consists of fragments of crystals that are already present in the solution, it is called true secondary nucleation. And when the seed is formed from crystals breaking due to collisions with other crystals, reactor walls, or impellers, it is called contact secondary nucleation (Perdikis, 1996). The interfacial energy between particles of the same composition and phase is generally relatively low, so the secondary heterogeneous nucleation occurs even at low values of S . (Hasson, 1981; Perdikis, 1996).

The nucleation can arise via several different mechanisms, depending on the degree of saturation and operating conditions. Primary homogeneous nucleation occurs only at higher levels of the saturation ratio, primary heterogeneous nucleation occurs at lower values of the saturation ratio, and secondary heterogeneous nucleation at even the lowest values of saturation ratio if there is seed present. This is presented in Figure 4, which shows a general plot of normalized nucleation rate vs. saturation ratio S (Perdikis, 1996).

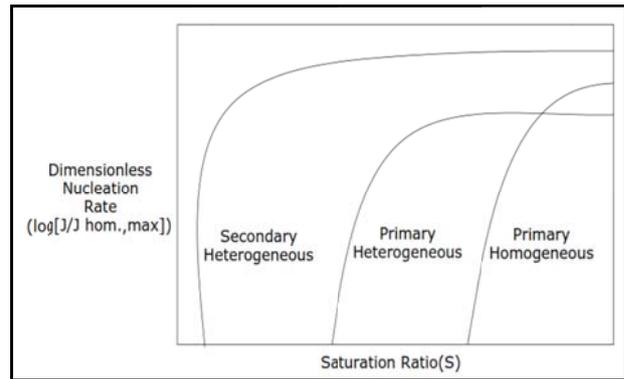


Fig. 4. Nucleation rate vs. saturation ratio S

As a result, it can be expected that primary heterogeneous nucleation would occur on the equipment surfaces, followed by secondary heterogeneous nucleation which would lead to a scale growth.

Crystal Growth

Crystal growth is critical to scale formation. It occurs via the incorporation of solvated solute molecules called growth nits, into step or bend sites on the crystal surface (Dirksen, 1991). The growth is accomplished by the eight-step process given in Figure 5:

- 1) Transport of the growth unit from the bulk solution to the crystal surface.
- 2) Adsorption on the crystal surface.
- 3) Lateral diffusion over the surface.
- 4) Attachment to a step.
- 5) Diffusion along a step.
- 6) Integration into the crystal at a bend site.
- 7) Diffusion of solvent molecules away from the crystal surface.
- 8) Release of heat of crystallization and its transport away from the crystal.

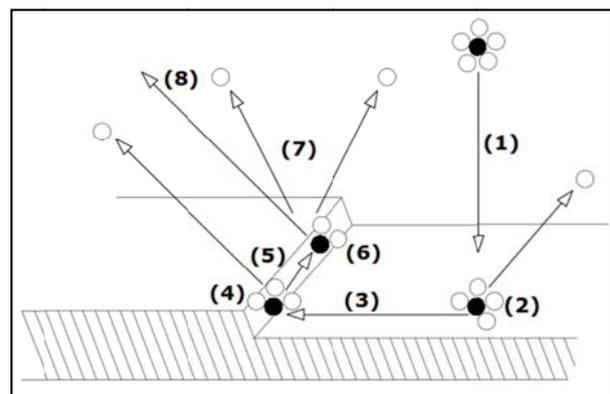


Fig. 5. Crystal growth stages

Besides the saturation ratio, there are some other factors that can affect crystal growth and thus, scale formation. These factors include temperature, matrix anion effects, impurity effects, presence of seed crystals and surfactants.

Conclusion

Based on the research studies carried out, it was found that as soon as formed on the industrial equipment surfaces, gypsum scale formations can only be effectively removed mechanically.

Regardless of the fact that the scale formation mechanism and the factors that affect it are identified, gypsum scale formation is inevitable when calcium-containing bases such as quicklime and slaked lime, and sulfuric acid are mixed.

Once the scale formation is deposited on the equipment surface, it becomes extremely impervious to chemical removal and is only removable by most established mechanical methods, which in general are labor-intensive and costly.

In order to find viable technological approaches for the elimination of gypsum scale formation during the pyrite flotation a comprehensive research study has been initiated. The study surveys both mechanical and chemical techniques for activation of depressed pyrite.

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