# Copper removal from oil-field brine by coprecipitation

Jafar Khosravi, Abdolmohammad Alamdari*

*Chemical and Petroleum Engineering Department, School of Engineering, Shiraz University, post code 7134851154, Shiraz, Iran*

## ARTICLE INFO

## ABSTRACT

The present study aims at investigation of copper removal from oil-field brine by coprecipitation process. The produced brine containing heavy metals is usually returned to the reservoir for water flooding or is discarded to the surroundings. Therefore, surface waters or underground waters may be polluted due to probable contact to these discarded waters. Removal experiments were carried out at room temperature in a bench-scale crystallizer equipped with a draft tube. In order to gain an insight into the influence of soluble compounds in the industrial natural brine on the precipitation process, some comparative experiments were performed both on a sample of natural brine and on a synthetic simulated brine in the absence of natural impurities. A metal removal practice by coprecipitation of copper through $CaCO_3$ precipitates induced by reaction of $Na_2CO_3$ and $CaCl_2$ reduced the copper concentration ($Cu^{2+}$) from 0.27 ppm in the synthetic brine to 0.06 ppm. This removal of 78% required only 1 g of precipitate per 0.15 mg copper metal. Analysis of the experimental results suggested that about 5% of the copper removal from the synthetic brine was through the mechanism of incorporation into the crystal lattice, and around 95% was through the adsorption on the crystal faces.

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## 1. Introduction

Heavy metals in different physical and chemical forms, usually detrimental to human and animal lives, are introduced to the environment due to human activities or natural phenomena [1]. Heavy metals are assigned to those having atomic weights more than 56, and they usually belong to intermediate elements in the periodic table [2]. Accumulation of heavy metals such as lead, nickel, chromium, copper and mercury in the body may cause disastrous consequences to human health. Effect of heavy metals, perhaps even in the range lower than permissible concentrations, on children is uncompensatable [1].

Oil-field brine has been reported to contain traces of Pb, Cu, Ni, Cr, Mn, Co, Hg, and Zn. Discharge of oil-field brine containing heavy metals to the environment, will pollute the surface waters and eventually will be hazardous to human life [3]. The conventional water treatment procedures usually are not able to effectively remove all pollutants from the surface waters. Therefore, the water consumers are continually exposed to the pollution by heavy metals.

Removal methods of heavy metals are categorized to biological and chemical procedures; in biological removal, heavy metals are absorbed by microbes and aquatic plants, while in the chemical methods such as ion exchange, adsorption, extraction, use of electrochemical cells, and precipitation, a kind of reaction is usually used to remove these materials [4]. The present study uses the coprecipitation process to remove the traces of copper from the oil-field brine. An abundance of calcium ion in the oil-field brine suggests that precipitation of calcium carbonate for metal removal would perhaps be economically promising. This compound which has a small value of solubility product is a good candidate in terms of saving in consumption of chemicals for coprecipitation process to remove metals from the brine. The most common natural minerals of calcium carbonate are calcite, vaterite, and aragonite. Generally, calcium carbonate is a safe chemical which its inhalation or contact with eyes seems harmless [5]. Sodium carbonate as feed material for producing calcium carbonate in the brine, on the other hand, is easily available and relatively cheap.

The characteristics of calcium carbonate precipitates will directly affect the efficiency of metal removal. Large particles of precipitation product may easily be settled and removed from the water, while non-uniform and fine particles usually encounter problems of low filtration efficiencies [6]. Characteristics of product particles depend on supersaturation, nature of particles in growth and nucleation mechanisms, mixing effects, etc. [6]. The location of feed entrance to precipitator is influential in size distribution of product particles. Beneath an impeller has been reported to be the optimum location for entering the feed streams [7]. Since the mixing intensity at the vicinity of the impeller is higher, pockets of feed streams quickly loose their identities there and mix with the bulk liquid. Concentration gradients between the pockets of liquid around the impeller are lower leading to reduction in local

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* Corresponding author. Tel.: +98 9171184316; fax: +98 711 6287294.
*E-mail addresses:* alamdari@shirazu.ac.ir, alamdari44@gmail.com (A. Alamdari).
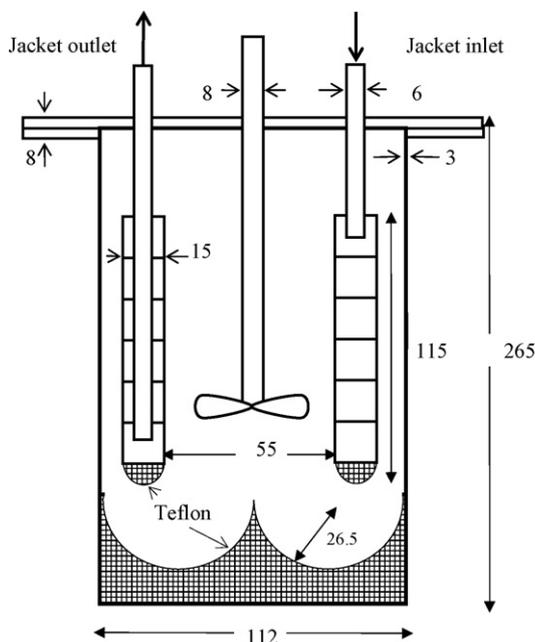
**Fig. 1.** Schematic diagram of the precipitator (dimensions are in mm).

supersaturation and hence reduction in nucleation. This reduction will result in generation of coarser product particles and ease of filtration.

Impurities may also be influential in size distribution of the product particles. For example, presence of $Mg^{2+}$ ions may reduce the growth rate of calcite by about 50% through the blockage of growth sites on the crystal faces [8]. The size of precipitates may also be influenced by heavy metals present in the water. Ions of $Cu^{2+}$ reduce growth of calcite due to generation of $CuCO_3$ and blockage of the active growth sites of calcite through adsorption of $CuCO_3$ on the sites [9]. The present study aims at investigating the removal of copper as a type of heavy metals from the oil-field brine through the coprecipitation process with calcium carbonate.

## 2. Experimental

Experiments were aimed at the examination of the $CaCO_3$ precipitation for metal removal, and studying the influence of parameters such as pH and mixing intensity on the removal efficiency. The influence of injection procedure of reactants on the size distribution of calcium carbonate product and the mechanism of metal removal by coprecipitation were also under consideration. Mechanism of metal removal will reveal if the metal is adsorbed on the surface of the calcium carbonate particles or is incorporated into the crystal lattice.

### 2.1. Experimental details

The following reaction was used to precipitate calcium carbonate in the oil-field brine.

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$$
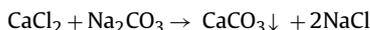
Experiments were carried out in a stainless precipitator equipped with a draft tube and four baffles. A stream of water from a bath was circulated inside the jacket fixed around the draft tube as shown in Fig. 1 in order to maintain the temperature of the solution in the precipitator at a constant value. The temperature of the solution was measured through a thermometer partly submerged in the solution inside the draft tube above the propeller. During the course of experiments the temperature was recorded several times.

Two sight glasses installed on the lid provided the observance of the precipitator contents and of the suspension flow circulation inside the draft tube. The rotational speed of the propeller was adjustable in the range 20–1500 rpm. A few holes provided on the lid were used for sampling and introduction of feed materials to the precipitator. The internal and external diameters of the draft tube were designed to minimize the change in flow speed inside and outside the tube. A sharp change in the flow speed may lead to a higher level of secondary nucleation. Additionally, on the bottom end of the draft tube a Teflon ring was fixed to modify the streamlines and to minimize turbulency and friction when the flow changes the direction. To avoid developing a stagnant region at the bottom and to make the streamlines of flow smooth, a Teflon block was machined so that a cone-shaped surface was mounted at the bottom of the crystallizer (Fig. 1). A 45°-pitched-6 blade propeller was used for circulation whereby the flow direction inside the tube was downward and outside the tube was upward.

The reactor was filled with 700 ml of synthetic oil-field brine and 200 ml of 2.5 M $Na_2CO_3$ solution. Then, the mixture was stirred for about 15 min and the pH of the solution was measured. The pH value after the addition of soda ash in the experiments was usually more than nine without adjustment. Using a syringe pump with a maximum capacity of 290 ml/h, 100 ml of 5-M-$CaCl_2$ solution was injected to the precipitator underneath the propeller with a rate of 150 ml/h. It took about 40 min to inject the calcium chloride solution.

The effect of seed addition on the metal removal was investigated by addition of an amount of $CaCO_3$ particles almost 20% of the product calcium carbonate to the solution before the commencement of the injection. At the end of the experiment the suspension was filtered and the filtrate was sampled for chemical analysis and determination of the metal removal efficiency. The filter cake from each experiment was washed and dried in an oven and the product particles were analyzed for size by the hydrometry method due to the experience that precipitate particles were less than 75 μm [10].

In order to understand that if the removed metal from the solution was adsorbed on the faces of precipitates or incorporated into the crystal lattice, the filter cake in a run first was washed with water and then dissolved in $HNO_3$ acid and the acid solution was analyzed for the metal concentration.

The synthetic solution containing 0.270 ppm $Cu^{2+}$ was prepared by dissolving 10.3 mg of copper (II) nitrate trihydrate, $Cu(NO_3)_2\cdot3H_2O$, with a purity of 99% and a molecular weight of 242 in 10 L of distilled water. The dilution was performed in two stages; first dilution to 1 L and second to 10 L using a 1000 ml volumetric flask. The reading errors of the digital scale and of the volumetric flask were $\Delta m = 0.1$ mg and $\Delta V = 0.5$ ml, respectively. Therefore, the relative errors in weight and volume measurements were $\Delta m/m = 10^{-2}$ and $\Delta V/V = 5 \times 10^{-4}$, respectively. Relative error propagated to concentrations was calculated as $10.5 \times 10^{-3}$ using the equation:

$$\frac{\Delta c}{c} = \frac{\Delta m}{m} + \frac{\Delta V}{V} \tag{1}$$

where $c$ is the copper concentration in the final solution, $m$ is the weight of copper nitrate trihydrate, $V$ is the volume of flask, and $\Delta$ denotes the corresponding random errors.

### 2.2. Chemical analysis

Copper concentration was measured using the method of ICP-ES, inductive coupled plasma-emission spectrometry [10]. In order to test if the ICP-ES instrument measures the $Cu^{2+}$ concentration correctly two samples of synthetic solution with known concentrations of $Cu^{2+}$ (0.270 and 10.000 ppm) were analyzed by the instrument. The measured values for both cases (0.267 and