Copper removal from oil-field brine by coprecipitation

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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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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, $Cu(NO_3)_2 \cdot 3H_2O$, 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 10.5×10^{-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 Δ 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

10.1 ppm) indicated a relative prediction error of around 1%. This relative error is almost identical to the relative error already calculated for the known solutions through Eq. (1).

2.3. Hydrometry method

Hydrometry, a standard method for size measurement of particles smaller than 75 μm, is based on the changes in the density of a suspension due to settling of particles [11]. Reliability of the hydrometry method for size measurement of $Mg(OH)_2$ particles has been reported in the literature [12]. Two almost identical samples of $Mg(OH)_2$ particles provided by multiple divisions have been measured by the methods of hydrometry and wet screening. The comparison of the results has shown a consistency of measurements by the two methods of size analysis.

All product particles from the precipitation experiments were transferred to a 1-L-cylinder. A volume of 125 ml of 4% sodium hexa-meta phosphate solution as dispersant was added to the cylinder contents. Then the distilled water was added until the suspension volume reached 1 L, and the suspension was well mixed using a stirrer. In another cylinder a volume of 125 ml of 4% hexa-meta phosphate solution was diluted with distilled water to 1 L and was considered for comparison. Two 152H type hydrometers were inserted in the solutions and readings were started. Readings from both cylinders were arranged to be implemented at times 0.5, 1, 2, 3, 4, 5, 10, 15, 30, 45, 60, 120, 240 and 1440 min. The size distribution of particles in terms of mass fraction oversize was calculated using the relevant relations in the hydrometry method [10]. It is pertinent to note that each measurement by hydrometry was performed three times and the average readings were calculated and used in the determination of oversize mass fractions. Comparison of two particle size distributions was made by comparing the mass mean size of one distribution with the mass mean size of another distribution. This was implemented to quantify the comparison and to avoid the report of several particle size distributions. The following equation was used to calculate the mass mean size of distributions:

$$d = \frac{\sum d_i w_i}{\sum w_i} \tag{2}$$

where d is the mass mean size of distribution, i is the counter of readings having a maximum value of 14, w_i and d_i are the weight fraction and average size of particles in the size interval i, respectively.

3. Results and discussion

3.1. Particle formation and size distribution

The mass mean size of distributions calculated from hydrometry results for $CaCO_3$ particles produced from the synthetic solution at pH around 10 and temperature around 23 °C in the presence of 0.270 ppm Cu^{2+} at various rotational speeds of stirrer are shown in Fig. 2. Results shown in Fig. 2 indicate that at rotational speed of 200 rpm the product has the largest mean size. It seems at rotation speeds less than the optimum 200 rpm the growth of $CaCO_3$ particles is limited by mass transfer from bulk to the surface of particles. Therefore, the supersaturation was not released mainly on growth, and nucleation level was raised in the solution leading to a smaller mass mean size. An increase in rotation speed more than the optimum 200 rpm increases the growth of particles but on the other hand increases the nucleation due to agitation. A high level of nucleation may neutralize the effect of growth on the mean size enlargement.

Since the calcium carbonate precipitation is an irreversible reactive crystallization process, the product yield is expected to be
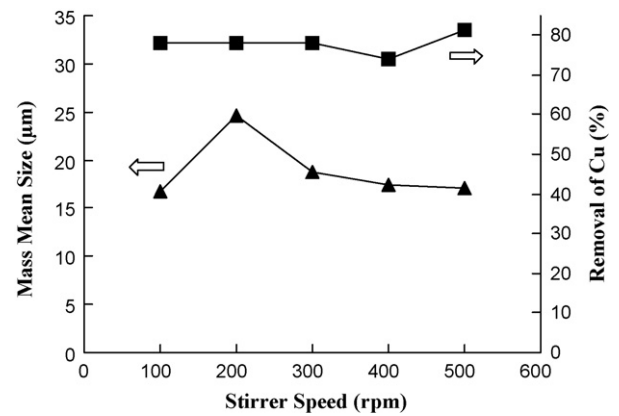
Fig. 2. The effect of rotational speed of stirrer on the mass mean size of precipitated $CaCO_3$ particles and on the removal of copper metal through the coprecipitation of $CaCO_3$ from a synthetic solution at 23 °C and pH around 10 when the initial concentration of Cu^{2+} was 0.270 ppm.

independent of agitation intensity and dependent only on the solubility product of $CaCO_3$.

Postulating that presence of initial seeds would decrease the primary nucleation, two comparative experiments were carried out in the absence and in the presence of enough initial seeds. The addition of initial seeds was ineffective in increasing the size of $CaCO_3$ precipitates. The mean size of precipitates produced in the presence and in the absence of initial seeds was 22.7 and 24.7 μm, respectively. The vague and insignificant effect of seed on the size distribution of product precipitates may be due to insufficient amount of seed used, or perhaps due to prominent influence of nucleation mechanism rather than growth on particle formation.

In another attempt, the injecting fluid and the fluid in the precipitator were replaced with each other; therefore, $CaCl_2$ was added instantaneously to the initial solution and then Na_2CO_3 was injected slowly. Comparison between results of this set of experiments showed that the mean size of particles was larger in the case of $CaCl_2$ injection. The mean size of particles for each case of injecting fluids of $CaCl_2$ and Na_2CO_3 was 24.7 and 18.56 μm, respectively.

It is pertinent to note that at the experienced rate of sodium carbonate injection the synthetic solution remained clear for about 5 min after the commencement of injection. This indicated that the rate of injection was low enough to prevent the primary nucleation, however, during the injection the pH of the solution increased significantly. A higher efficiency of copper removal (78% against 59%) was resulted when $CaCl_2$ was the injecting fluid. The enhancement in removal efficiency was seemingly due to the performance of coprecipitation at a higher pH. However, when $CaCl_2$ is the injecting fluid and Na_2CO_3 is in excess in the solution, the concentration of $CO_3{}^{2-}$ anions around the particles seem to be more due to their incorporation in the crystal lattice. These negative ions cause higher concentration of Cu^{2+} cations around the particles and thereby higher probability of metal incorporation in the lattice or adsorption on the surface. In case of Na_2CO_3 injection when $CaCl_2$ is in excess in the solution the concentration of Ca^{2+} cations around the particles seems to be high repelling the metal ions of Cu^{2+} and reducing the possibility of their incorporation or adsorption. When Na_2CO_3 was the injecting reactant, the metal removal reduced to about 59% and the minimum concentration of copper was 0.11 ppm.

3.2. SEM observations

Figs. 3–5 show that calcium carbonate crystals precipitated in the experiments carried out in the present study. Fig. 3 illustrates different types of $CaCO_3$ crystals precipitated from the industrial
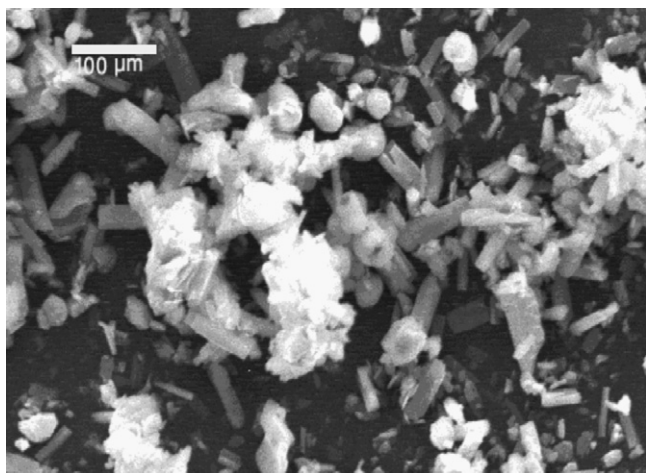
Fig. 3. Representative photomicrograph showing calcium carbonate particles precipitated from an industrial natural brine solution containing 0.27 ppm Cu^{2+} at the agitation speed of 200 rpm, when $CaCl_2$ was the injecting reactant.
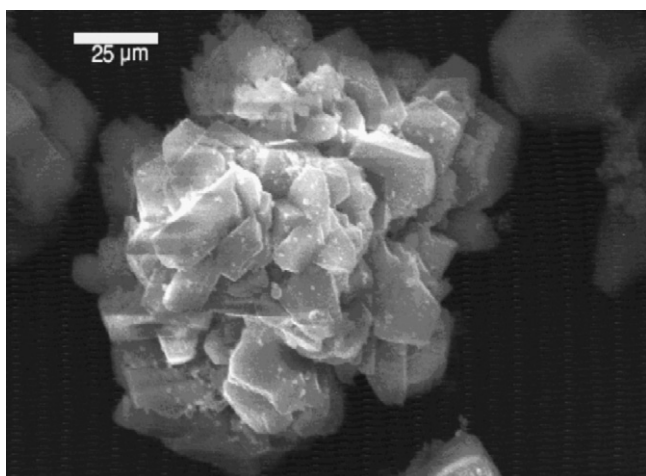

Fig. 4. Representative photomicrograph showing calcium carbonate particles precipitated from the synthetic solution in the presence of 0.270 ppm Cu^{2+} at the agitation speed of 200 rpm when $CaCl_2$ was the injecting reactant.
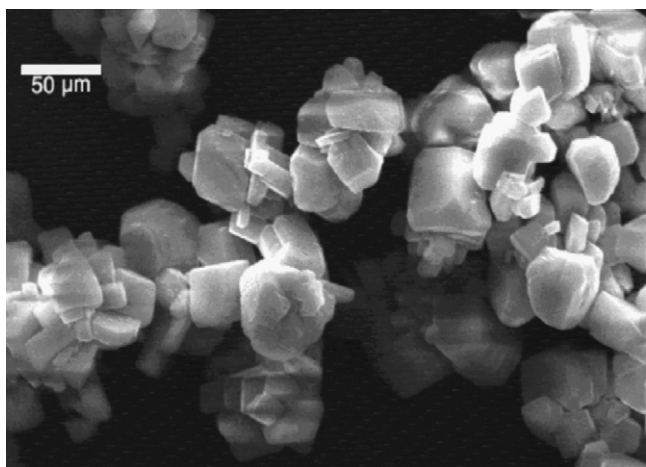

Fig. 5. Representative photomicrograph showing the calcium carbonate particles precipitated from the synthetic solution in the absence of copper metal at the agitation speed of 200 rpm when $CaCl_2$ was the injecting reactant.
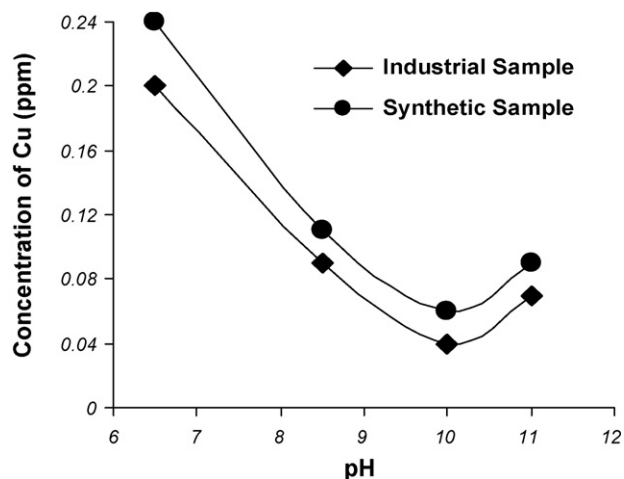
Fig. 6. Comparison of metal concentrations after removal treatments through the coprecipitation with $CaCO_3$ at 23 °C from the synthetic and industrial solutions of oil-field brine at different pH values, when $CaCl_2$ was the injecting reactant.

oil-field brine. However, Fig. 5 showing $CaCO_3$ crystals precipitated from the synthetic brine suggests only one type of crystals. Comparison of the photomicrographs of $CaCO_3$ crystals shown in Figs. 3–5 with the photomicrographs of calcite, aragonite and vaterite shown in references [7,13] indicates that the crystals precipitated from the synthetic brine are calcite.

3.3. Copper removal from synthetic solution

As shown earlier the stirrer rotational speed is influential in the mass mean size of product particles, but is almost ineffective on the removal efficiency of metal from the synthetic oil-field brine sample (Fig. 2). As Fig. 2 shows the largest and the smallest mean size values of $CaCO_3$ particles precipitated from the synthetic brine solution is 24.7 and 17 μm, respectively. The enlargement of product particles due to optimizing the variables such as stirrer speed is not so extensive to change dramatically the surface area available for adsorption or incorporation of Cu^{2+} ions; therefore, the removal efficiency is not much influenced by the intensity of agitation.

The optimum value of pH for metal removal was experienced as 10 for both cases of synthetic and industrial brine solutions (Fig. 6). Several experiments were carried out with different amounts of reactants to determine the optimum amount of precipitates necessary for removal of specified metal concentrations. For a solution volume of 700 ml at pH of 10 and rotational speed of 200 rpm, use of more than 0.01 mol of each reactant resulted in the same level of metal removal. This set of experiments leads to treating 1000 ml of oil-field brine containing 0.270 ppm copper metal with reactants equivalent to 1.4 g $CaCO_3$ to remove about 78% of the copper. This corresponds to removal of 0.15 mg of copper metal with 1 g $CaCO_3$ precipitates.

Chemical analysis of samples taken during the course of experiment showed that 67% of the metal was removed after the addition of one third of the $CaCl_2$ solution and 74% of the metal was removed

Table 1
Depletion of copper concentration with injection of $CaCl_2$ in the synthetic solution at the stirrer rotational speed of 200 rpm, pH of 10, and temperature of 23 °C, when $CaCl_2$ was the injecting reactant.

Hypothetical concentration of $CaCl_2$ (g/L)	Concentration of Cu (ppm)
0.0	0.27
16.65	0.09
38.85	0.07
55.5	0.06

Table 2
Sample analysis of an industrial oil-field brine from a local field before and after treatment with Na_2CO_3.

Ion	Concentration before treatment (mg/L)	Cumulative concentration before treatment (eq/L)	Concentration after treatment (mg/L)	Cumulative concentration after treatment (eq/L)
Ca^{2+}	20800	1.04	–	–
Mg^{2+}	5586	1.506	5586	0.466
Na^+	69055	4.508	92975	4.508
Fe^{3+}	570	4.538	570	4.538
HCO_3^-	1332	0.022	1332	0.022
SO_4^{2-}	800	0.038	800	0.038
Cl^-	159750	4.538	159750	4.538

after the addition of two third of the $CaCl_2$ solution. This suggests that as the particles of $CaCO_3$ form and grow, the metal species are adsorbed on the particles or are trapped inside the body of the particles. Table 1 shows the copper concentration in the solution during the course of removal experiment. The hypothetical concentration of $CaCl_2$ was used to resemble the consumption of $CaCl_2$ reactant for each unit volume of brine.

Another experiment was carried out to separate the contributions of incorporation and adsorption mechanisms. Contact of $CaCO_3$ precipitates with solution containing metal was implemented in two stages; first, addition of already prepared initial seeds which can remove metal solely through the adsorption and second, production of freshly precipitating particles in the metal containing solution by reaction which can remove metal through both adsorption and incorporation. At the first stage, a mass of particles equivalent to 0.01 mol of $CaCO_3$ was precipitated through a reaction in the absence of copper metal and was introduced to the metal containing solution as initial seed. These initial seeds were around 20% of the $CaCO_3$ particles which would be used on the whole in the removal experiment. At the second stage, the remainder 80% of particles was produced through the precipitation reaction in the solution containing metal. Therefore, the sum of initial seed particles and particles produced by precipitation was the same with the case when all the $CaCO_3$ particles were produced by the reaction in the presence of metal.

The two cases of using already prepared initial seed particles to adsorb metal on their surface and freshly precipitating particles in the brine solution were compared for their tendency to deplete the metal concentration in the solution. Use of already prepared initial seed particles resulted 74% removal and reduced the metal concentration to 0.07 ppm (from 0.270 ± 0.003 ppm) after 40 min of stirring. The final depletion in the metal concentration for the case of injecting $CaCl_2$ and Na_2CO_3 reactants and freshly precipitating $CaCO_3$ particles in the solution was 0.06 ppm (from 0.270 ± 0.003 ppm) with a removal of 78%. The absolute error of ± 0.003 was calculated by multiplying the relative error already calculated for the known samples (1.05×10^{-2}) by the value of concentration.

Results of this experiment suggest that fresh particles precipitated through the reaction remove more metal than already prepared initial seed particles. Therefore, it is postulated that freshly precipitating particles remove copper through both mechanisms of surface adsorption and incorporation in the crystal lattice, but already prepared initial seed particles remove metal through the adsorption on the sites still active on their surfaces.

Thus, it may be concluded that around 5% of metal removal is through the mechanisms of incorporation into the crystal lattice or trapping in the agglomerates and around 95% of the metal removal is through the mechanism of adsorption on the particle surface.

3.4. Metal removal from industrial brine solution

Total dissolved solid (TDS) in a sample of oil-field brine from a local oil-field in South Iran was estimated as 247.2 g/L through the gravimetric analysis after evaporation to bone dryness and the copper concentration in this sample was measured as 0.270 ppm. The final concentration of copper in the industrial brine after treatment by coprecipitation with $CaCO_3$ at pH = 10, $T = 23\,°C$, and stirrer speed = 200 rpm was 0.04 ppm indicating a removal of 85%. The color of the industrial brine changed to milky by addition of the first drop of the sodium carbonate solution. Addition of Na_2CO_3 increased the pH in both cases of synthetic and industrial solutions; however, pH increase was less in case of the industrial solution.

The copper incorporated into the crystals of $CaCO_3$ precipitated from the industrial oil-field brine was 14×10^{-6} g/g solid. This was determined by wash treatment of crystals and their dissolution in HNO_3. It is expected that the wash treatment removed the adsorbed metal from the crystal surface; and therefore, it is deduced that the remaining metal content incorporated into the crystal lattice.

Comparison of masses precipitated from the industrial brine solution and from the synthetic solution showed that precipitated mass from the industrial solution was almost triple in amount of that from the synthetic solution. A comparison was also made in metal removal from the synthetic and the industrial solutions under the same conditions. Fig. 6 shows that metal removal through the precipitation from the industrial solution is more than the removal from the synthetic solution. This seems to be due to more precipitate mass separated from the industrial brine and more chance of metal adsorption on the particle surface or of metal incorporation into the crystals.

Table 2 shows the equivalent concentrations for the principal ions in the oil-field brine sample from South Iran before and after treatment. Using data from this table the possible compounds in the sample were predicted as shown in Table 3. It is pertinent to note that the concentrations of copper metal compared to other cations are negligible; therefore, the tables exclude the copper concentrations.

The molar concentrations of Ca^{2+} and CO_3^{2-} in the solution after injection of reactants which were calculated using K_{sp} of $CaCO_3$ (4.5×10^{-9} at 25 °C) are 2.68 and 4.02 mg/L, respectively. Solubility product of $CaCO_3$ at 25 °C has been reported in the range $K_{sp} = 3.7 \times 10^{-9}$–$8.7 \times 10^{-9}$ [9]. These concentrations were not shown in the tables due to their negligible values compared to the concentrations of other compounds such as NaCl and $Mg(HCO_3)_2$.

Table 3
The conceptual compounds in an oil-field brine sample from a local field before and after treatment.

Compound	Concentration (eq/L) before treatment	Concentration (eq/L) after treatment
$Ca(HCO_3)_2$	0.022	–
$Mg(HCO_3)_2$	–	0.022
$CaSO_4$	0.016	–
$MgSO_4$	–	0.016
$CaCl_2$	1.002	–
$MgCl_2$	0.466	0.428
NaCl	3.002	4.042
$FeCl_3$	0.03	0.03

4. Conclusions

A copper removal practice by coprecipitation with $CaCO_3$ carried out in the present study reduced the copper concentration in a synthetic sample of oil-field brine from 0.270 ppm to about 0.06 ppm. A removal of 78% required only 1 g of precipitate per 0.15 mg copper metal. Ease of filtration of $CaCO_3$ particles from the brine is a privilege of the coprecipitation process.

Mixing intensity was found to be influential in particle size distribution development of $CaCO_3$ particles precipitated from synthetic oil-field brine through the reaction of soda ash with $CaCl_2$. The largest average size of particles (24.7 μm) was generated at a mixing intensity of 200 rpm. However, the use of initial seeds did not improve the size distribution and was ineffective in size enlargement of the precipitates seemingly due to prevalence of primary nucleation in the precipitation of $CaCO_3$.

The arrangement of reactant addition to the brine was influential in both the particle enlargement of precipitates and the removal efficiency of copper from the brine. When soda ash was instantaneously added to the brine and the calcium chloride solution was injected slowly larger particles were precipitated and copper was removed more efficiently. Analysis of the experimental results indicated that about 5% of the copper removal from the brine was through the mechanism of metal incorporation into the crystal lattice, and around 95% was through the mechanism of metal adsorption on the crystal faces.

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