

Investigation of Solvay Process Waste Sludge Potential for Precipitation of Heavy Metals from Aqueous Solutions

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Abstract-- Industrial plants producing light and dense soda ash generate significant amounts of effluents which have been globally recognized as an environmental problem. Waste liquid streams from soda production plant in Bosnia and Herzegovina are discharged to several settling basins, one of which is completely filled. Considering the high content of CaCO_3 and Ca(OH)_2 and the resulting high pH value of the waste material in filled settling basin, the effect of the solid phase of the material on the chemical precipitation of heavy metal ions from their aqueous solutions was investigated in this paper. The results obtained in this study showed it is possible to remove more than 99.9% of lead, zinc, nickel and copper from their monocomponent aqueous solutions of initial concentrations of 500 mg/l, which may contribute to the consideration of alternative uses of waste material from the soda production process as well as its subsequent disposal in an adequate manner.

Index Term— Solvay process, waste sludge, water treatment, heavy metal precipitation

I. INTRODUCTION

Various chemical, mining, steel, fertilizer, paper, and pulp industries generate huge amounts of wastes out of their production processes (1). An example of a strong impact on natural waters includes the plants producing light and dense soda ash, belonging to the chemical industry (2). Soda ash in the EU is almost entirely manufactured by the Solvay process (also called the ammonia soda process), using the locally available salt brine and limestone of the required quality (3). Waste effluents from the soda production process have been globally recognized as an environmental problem, resulting in many published works related to the modification of the production process, or the alternative use of waste by-products (4, 5, 6, 7, 8).

For the purpose of supplying industrial water, the soda production plant in Bosnia and Herzegovina uses two types of resources: fresh water from the nearby reservoir of Lake Modrac, and salt water transported by pipes from a salt mine. In a soda factory, fresh water is used: for cooling

water in production processes, for steam production and for chemical treatment of water.

The treatment of raw lake water requires correction of turbidity and suspended matter content, which is envisaged by a filtration process in sand filters and then removal of calcium carbonates and bicarbonates from water by the addition of Ca(OH)_2 and Na_3PO_4 to water. The lime sludge that is generated is cream colored and contains a certain amount of aluminosilicates (clay and sand particles) originating from lake water. Brine is obtained by pumping fresh water into the boreholes of a salt mine, in which water dissolves salt. Brine of industrial concentration is transported from the reservoir by pipeline to the soda production plant. Brine treatment is carried out in the soda factory by adding Ca(OH)_2 and Na_2CO_3 to water. The lime sludge that forms as a by-product is white in color and contains a large amount of chlorides derived from salt water.

Lime sludges from brine and fresh water treatment processes, together with waste water from ammonia distillation and other factory wastewaters (resulting from machine cleaning and facility washing), are transported through the collecting pipeline to four settling basins with a total area of approximately 560,000 m², and the material in these settling basins is known as the *white sea*. Each of these settling basins has a drainage system for draining water, as well as a system of overflow pipes on the surface of the basins, to separate the solid phase from the water.

It has been estimated that millions of tons of sludge have been deposited in settling basins since 1979, of an average composition dominated by the limestone component - CaCO_3 , which so far has not found application (9). The settling basin No. 1 is currently 100% filled and no longer operational, which raises the question of resolving its waste material. In some cases, waste materials generated from other industrial processes may act as reagents. An example of this is lime sludge. Wirojanagud et al. (10) used waste lime sludge from cellulose and paper production for the chemical precipitation of heavy metals from water, and the results of their study showed that precipitation of heavy

metals by lime sludge was effective, as indicated by the removal efficiency of 90% for Pb, Cd and Hg, and 100% for Cr.

Considering the high content of CaCO_3 and Ca(OH)_2 and the resulting high pH value of the material in settling basin No. 1, the effect of the white sea solid phase on the chemical precipitation of heavy metal ions from their aqueous solutions was investigated in this paper.

II. EXPERIMENTAL PART

2.1. Materials

The following chemicals were used in this study: $\text{Pb(NO}_3)_2$, min. 99.5 %; $\text{Zn(NO}_3)_2 \cdot 10\text{H}_2\text{O}$, min. 99%; $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, min. 99%; $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$, min. 99.5%; lead standard solution, 1,000 mg/l Pb in 0.5 M nitric acid (from $\text{Pb(NO}_3)_2$); zinc standard solution, 1,000 mg/l Zn in 0.5 M nitric acid (from $\text{Zn(NO}_3)_2$); nickel standard solution, 1,000 mg/l Ni in 0.5 M nitric acid (from $\text{Ni(NO}_3)_2$); copper standard solution, 1,000 mg/l Cu in 0.5 M nitric acid (from $\text{Cu(NO}_3)_2$); nitric acid (HNO_3) 65%; demineralized water ($< 1 \mu\text{S cm}^{-1}$).

The *white sea* material from sediment basin No. 1 was spread over a flat, so that the thickness of its layer was approx. 2 cm and then passively dried at room temperature (approx. 21 °C) for 15 days. The dried material was ground to 0.01-0.25 mm of particles diameter, after which the moisture content in material was determined by drying at 105 °C. The dried and ground material was used as a precipitant of heavy metals lead, zinc, nickel and copper from their monocomponent aqueous solutions of an initial concentrations 500 mg/l.

Determination of the chemical composition of the prepared precipitant was performed by X-ray fluorescence spectrometry (XRF), BAS EN 15309:2010 method, using a S8 TIGER 4K spectrometer.

2.2. Precipitation experiment

By mixing the appropriate amounts of selected standard metal solutions and demineralized water, monocomponent aqueous solutions of lead, zinc, nickel and copper were obtained, with initial concentrations of 500 mg/l. Chemical precipitation of heavy metals in water was carried out batchwise under laboratory conditions at room temperature (average temperature 21.3 °C), by pipetting 100 ml of a heavy metal aqueous solution into a 250 mL laboratory glassware beaker, followed by the addition of an appropriate mass of precipitant and stirring with a magnetic stirrer, 300 rpm for 5 minutes. At the end of the given mixing time, the liquid sample was filtered through Whatman® quantitative filter papers 125 mm in diameter, first through a black ribbon circle and then through a blue ribbon circle, to separate the precipitated solid phase from the liquid one. All samples were stored in polyethylene bottles. The determination of heavy metals in aqueous solutions by

flame atomic absorption spectrometry (F-AAS) was performed using a Perkin Elmer Analyst 200 instrument. Prior to analysis, samples were filtered (black and blue ribbon circles) and 0.2 ml of concentrated nitric acid was added to each sample to adjust the pH of the sample and dissolve any residual heavy metal precipitates. A series of solutions of analyte of known concentrations was prepared in 25 ml volumetric flasks, pipetting exactly known volumes of stock analyte and diluting with 0.03 M nitric acid solution to the mark on the flask. A 0.03 M nitric acid solution was used as a blank. By measuring a series of solutions of known concentrations of the analyte, a calibration diagram was constructed, on the basis of which the analyte concentration in the sample was determined. Based on the results of the analysis of the content of heavy metals in water samples before and after precipitation and filtration, the efficiency of precipitation of heavy metals was calculated according to the equation:

$$E_r = \frac{C_0 - C_1}{C_0} \cdot 100$$

where:

C_0 - initial concentration of heavy metal in water (mg/l),

C_r - residual concentration of heavy metal in water (mg/l).

III. RESULTS AND DISCUSSION

In the dried sample of white sea, used as a precipitant, an average moisture content of 2.2% was determined. Table I shows the results of the chemical composition analysis of the precipitant using X-ray fluorescence spectrometry.

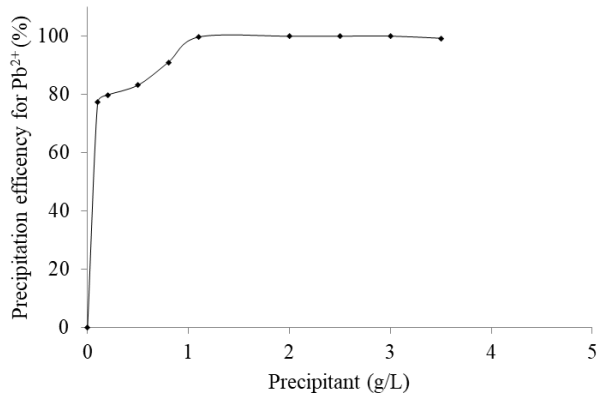
Table I
Results of the chemical composition analysis of the dried material White Sea by XRF method

Chemical species	Content (%)
CaO	58.131
Cl	12.5726
Na_2O	3.9059
SiO_2	2.558
MgO	2.2742
Fe_2O_3	1.4337
SO_3	1.2014
Al_2O_3	1.008
P_2O_5	0.0822
K_2O	0.068
SrO	0.0335
MnO	0.025

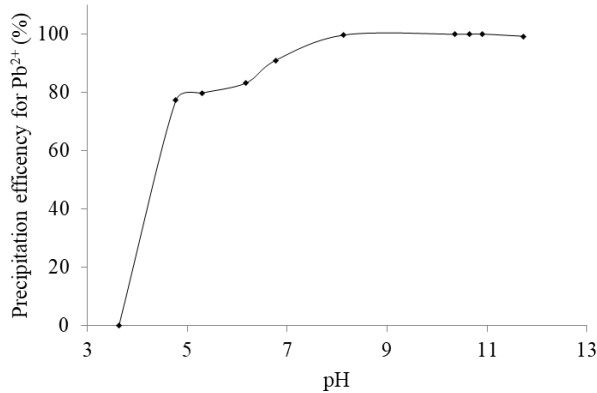
Figures 1 to 4 show the results of the precipitation efficiency of heavy metal ions in their aqueous solutions of an initial concentration of 500 mg/l, depending on the added

amount of precipitant and the pH conditions of the aqueous solution treated.

Upon addition of the precipitant, the pH of the treated aqueous solutions increases, and CaCO_3 from the precipitant reacts with heavy metal ions to form metal carbonates. In addition to metal carbonate, metal hydroxide can also be generated, due to the decomposition of calcium carbonate present in the precipitate into a carbonate ion, which in reaction with water can further give a hydroxide ion (11). The results of the experiment showed that to achieve a Pb^{2+} precipitation efficiency of 99.616%, a precipitant dose of 1.1 g/l was required, while significantly higher amounts of precipitant were required to further increase the efficiency (Fig. 1-a). It was also found that most of the total lead content was precipitated by raising the initial pH of the solution (3.63) to a value of 4.77 (Fig. 1-b). Further increases in pH resulted in a weaker increase in the efficiency of Pb^{2+} precipitation. Maximum lead precipitation efficiency (99.943%) was obtained by the addition of 3 g/l of precipitant, with the pH of the treated solution being 10.90.

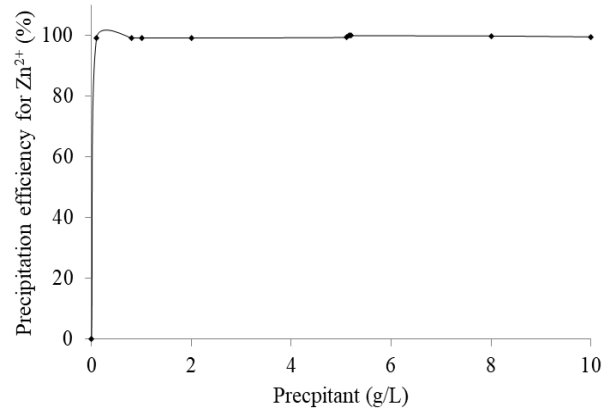


a)

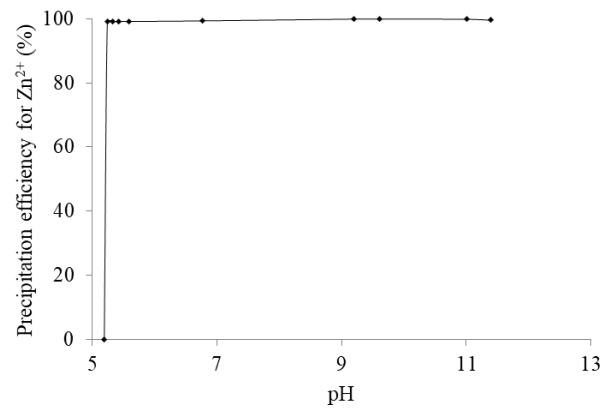


b)

Fig. 1. Precipitation of Pb^{2+} ions from their aqueous solution of initial concentration of 500 mg/l, depending on a) the added mass of the dried sample *white sea* and b) the pH of the solution

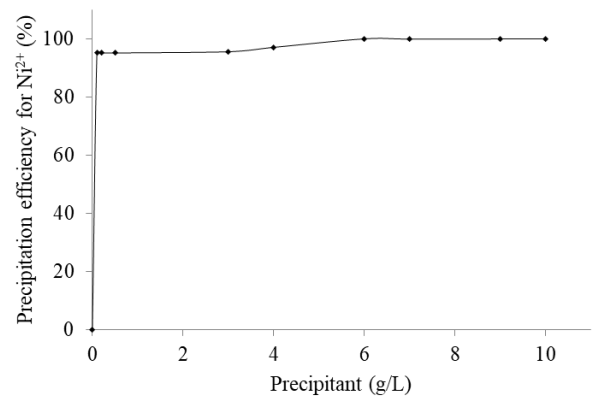


a)

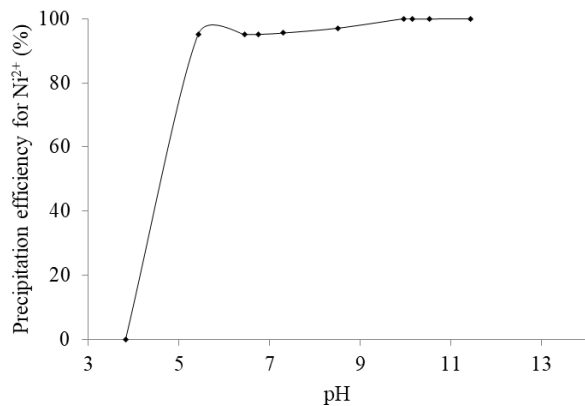


b)

Fig. 2. Precipitation of Zn^{2+} ions from their aqueous solution of initial concentration of 500 mg/l, depending on a) the added mass of the dried sample *white sea* and b) the pH of the solution

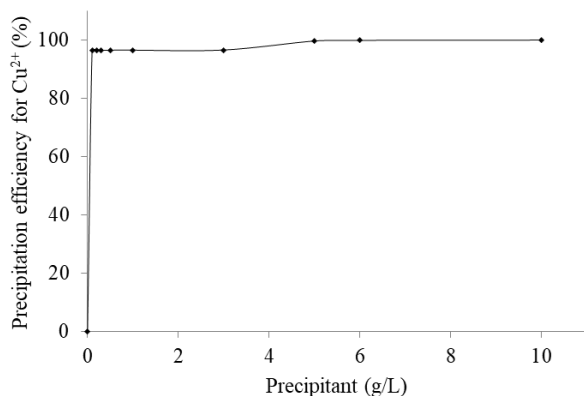


a)

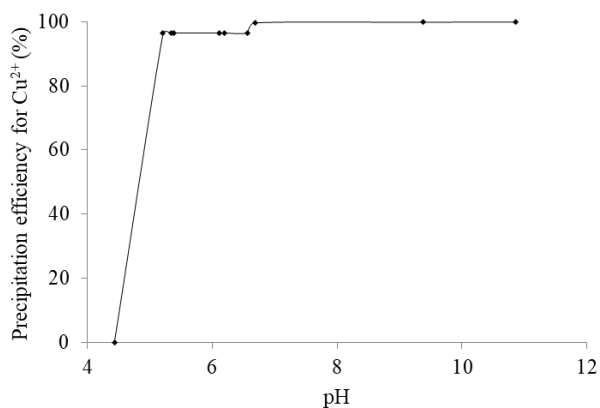


b)

Fig. 3. Precipitation of Ni²⁺ ions from their aqueous solution of initial concentration of 500 mg/l, depending on a) the added mass of the dried sample *white sea* and b) the pH of the solution



a)



b)

Fig. 4. Precipitation of Cu²⁺ ions from their aqueous solution of initial concentration of 500 mg/l, depending on a) the added mass of the dried sample *white sea* and b) the pH of the solution

Wirojanagud et al. (10) determined a pH of 10.70 for a sample in which they achieved maximum precipitation of lead ions (94.6%) from an aqueous solution of an initial concentration of 1433.7 mg/l using a paper industry waste

sludge. Upon the addition of the precipitant in an amount of 3.5 g/l, a residual Pb²⁺ concentration of 4.049 mg/l was detected at a pH 11.73 of treated solution. This phenomenon can be explained by the re-dissolution of amphoteric lead hydroxide.

When a precipitant of 0.1 g/l was added to an aqueous solution of Zn²⁺, the precipitation efficiency of zinc was 99.137% (Fig 2-a), which was 21.939% higher than the lead precipitated with the same dose of precipitant. The zinc hydroxide solubility curve shows a lower degree of solubility with respect to lead hydroxide (12), which favors the precipitation of zinc. The higher precipitation efficiency of zinc can also be explained by the initial pH of its aqueous solution, whose value (5.19) was higher than the initial pH of the water solution of lead (3.63), which made the added precipitant increase the pH of the zinc solution to a higher value than that obtained by the same mass of precipitant in the case of Pb²⁺, thereby improving precipitation.

It can also be observed that the largest part of the zinc precipitation was obtained in the pH range from the initial value of 5.19 to the pH value 5.24 of the treated solution (Fig. 2-b) and was 99.137%. By further increasing the dose of the precipitant, the increase in the pH of the solution and the efficiency of zinc precipitation were very small. According to Peters and Bhattacharyya (13), some metals such as zinc do not precipitate readily.

Compared to zinc, nickel had a lower efficiency of precipitation at lower pH values, until the pH of the treated solution was 9.95, above which residual Ni²⁺ concentrations in water solutions were lower than Zn²⁺. According to the literature data (14), nickel hydroxide has a lower solubility than zinc hydroxide at pH values > 9.

Most of the copper in its aqueous solution precipitated in the pH range from the initial value of 4.43 to the value of 5.21, with a precipitation efficiency of 95.093% (Figure 4-b).

The highest efficiency of precipitation of Cu²⁺ (99.93%) was achieved by precipitant dose of 10 g/l, wherein the pH of the treated solution was 10.86. Using lime sludge as precipitants, Sthiannopkao and Sreesai (11) achieved a lower copper solubility in water when the pH was around 9.5-11.

Overall results of waste material from the sedimentary basins of the factory for production of soda show significant potential for precipitation of heavy metals. This opens up the possibility of alternative use of the *white sea* material. Precipitating potential is also important in predicting the mobility of heavy metals in the subsequent disposal of a material after its use as a precipitant. The results of contents of Ni, Pb and Zn in 100-year-old solid waste produced by the soda ash plant in Jaworzno and their distribution pattern in the waste samples and soil profiles led to the conclusion that despite enrichment of heavy metals in the uppermost horizon on the top of the heap, the relation of historical production of soda ash in Jaworzno to current contamination of the local soil environment is insignificant (15).

IV. CONCLUSION

The addition of the White Sea as a precipitant to aqueous solutions of heavy metals results in an increase in the pH of the solutions and the precipitation of metals in the form of carbonates and hydroxides. The precipitation of heavy metals from their aqueous solutions depends on both the pH of the solution being treated and the type of metal that precipitates. By using the White Sea material as a precipitant, it is possible to remove more than 99.9% of lead, zinc, nickel and copper from their monocomponent aqueous solutions of initial concentrations of 500 mg/l, with an optimal pH value of the treated solutions in the range of 9.61 - 10.86. However, treatment of aqueous solutions of metals with the White Sea precipitant to extremely high pH values (> 11) can lead to the re-dissolution of amphoteric metal hydroxide precipitates, such as lead and zinc hydroxides.

The results obtained in this study may contribute to the consideration of alternative uses of waste material from the soda production process as well as its subsequent disposal in an adequate manner.

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