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Precipitation behaviour in pH adjusted lateritic ore solution

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Abstract

Hydrometallurgical procedure and chemical measurements were employed to study the precipitation behavior of different metals in a lateritic ore pregnant leach solution (PLS). Lateritic ore was leached in 1 M H₂SO₄ solution at 70 °C by standard leaching process. The leachate was afterwards subjected to the pH adjustment that led to the removal of metal ions by precipitation. Measurements of pH as well as chemical analysis show characteristic values of metal ion removal from the PLS.

Keywords: Cobalt; hydrometallurgy; acidic leaching

Izvod

Hidrometalurški postupak luženja lateritne rude uz hemijske analize u rastvoru luženja su korišćeni kako bi se ispitalo ponašanje različitih metala u koncentrovanom rastvoru luženja (PLS). Lateritna ruda podvrgnuta je standardnom postupku luženja u rastvoru 1 M H₂SO₄ na 70 °C. Iz dobijene lužine su nakon toga taloženi joni metala tokom menjanja pH vrednosti prvobitnog PLS rastvora. Rezultati merenja pH, kao i hemijskih analiza dali su karakteristične vrednosti na kojima je moguće iz PLS rastvora odstraniti određene jone metala.

Ključne reči: kobalt; hidro-metalurgija; kiselo luženje

Introduction

Cobalt and nickel are gaining more importance in key-future industries [1]. Cobalt is essential to manufacturing of Li-ion batteries, that find wide usage in all electrical applications, especially in fast growing market of electric vehicles [2]. Nickel demand is expected to grow rapidly in the next decades, mainly due to rising demand for high tech steels and Ni based alloys, that find broader application in industry, due to their extraordinary corrosive and high temperature properties [3].

Main source of these metals are lateritic ores [4]. These oxidic ores are commonly processed by a hydrometallurgical process route. This process includes acidic leaching and multiple following precipitation steps, in order to obtain a purified Cobalt hydroxide, or more common Nickel-Cobalt-hydroxide [5]. The obtaining of this requires deep knowledge about the precipitation behavior of the PLS of lateritic ore. This was the motivation for the studies done in this paper.

Experimental and materials

Lateritic ore from Indonesia was leached in standard leaching route. The chemical composition of the examined ore concentrate is given in Table 1.

Table 1: Lateritic ore - Complex ore concentrate composition

SiO ₂	MgO	Fe ₂ O ₃	NiO	Al ₂ O ₃	CaO	Cr ₂ O ₃	CuO	Co ₃ O ₄	K ₂ O	TiO ₂
%	%	%	%	%	%	%	%	%	%	%
11.7	5.81	70.7	3.80	4.27	0.13	1.78	<0,01	0.05	0.02	0.07

Leaching of lateritic ore was performed in a standard glass vessel, with stirring unit and cooler. The flask was placed inside of a temperature controlled heating unit (SAF Wärmetechnik GmbH, Weinheimer Str. 2A, 69509 Mörlenbach, Germany). Temperature was kept constant at 70 °C for 2 h. The lateritic ore was leached with 1M H₂SO₄ at a stirring speed of 300 rpm. Liquid to solid ratio of the leaching was 5:1. After the leaching process, filtering was done using vacuum filters. In total, 1000 ml of PLS was obtained.

During the addition of NaOH, pH-value, measured by a pH meter (Mettler Toledo, 1900 Polaris Pkwy, Columbus, OH 43240, USA) and potential, measured by a potentiometer (Xylem Analytics Germany Sales GmbH & Co. KG, Dr.-Karl-Slevogt-Str. 1, 82362 Weilheim, Germany), were constantly monitored. Visible changes in colour and precipitation of the solution were recorded. Addition of 10 M NaOH was done with µl pipettes under constant stirring of 300 rpm. Samples were taken at different pH values of the solution. Chemical analysis of the samples was performed using ICP-OES.

Results and discussion

Chemical analysis of the PLS show high leaching efficiency for cobalt and nickel, with 31 % and 17 % respectively. Meanwhile leaching of Iron and Chromium is kept low, which is desirable for this process. A full overview of leaching efficiency for the lateritic ore *at 70°C in 2 hours* can be found in **Table 2**.

Table 2. Leaching efficiency overview at 70°C in 2 hours

Element	Ni	Co	Al	Mn	Cr	Fe
Concentration in mg/l	1020	22.6	609	177	60.5	5850
Leaching efficiency in %	17.06	30.77	13.47	15.65	2.48	5.91

As for atmospheric leaching, results can be seen as satisfying, since highest leaching efficiencies were achieved for the desired metals, being Cobalt and Nickel.

Chemical analysis of the PLS are shown in **Table 3**. Initial pH of the solution after acidic leaching being 0.5.

Table 3: Chemical analysis of the PLS at different pH

<i>pH</i>	Ni mg/l	Co mg/l	Al mg/l	Mn mg/l	Cr mg/l	Fe mg/l
0.5	1020	22.6	609	177	60.5	5850
1.6	988	19.8	669	158	50.3	4370
2	956	19.6	620	150	49.9	4530
2.5	917	18.9	582	146	33.4	2400
2.8	918	19.1	602	145	8.79	514
5.8	653	14.7	15.8	124	2.01	112
7.2	112	4.3	3.36	111	< 0.3	23.1
8.4	9.75	0.51	1.3	26.7	< 0.3	6.8
8.5	9.06	0.3	4.86	1.98	0.45	36.8
9.9	2.5	0.3	1.5	0.57	< 0.3	7.6
12.8	0.24	0.3	13.0	0.12	1.02	3

The chemical analysis of the PLS at different pH-values shows a different reaction behavior than one would expect looking at the Pourbaix diagrams for the analysed metals. It can be stated, that precipitation of iron is taking place at lower pH, in comparison to Pourbaix [6]. On the opposite, precipitation of nickel is observed at higher pH in comparison to Pourbaix diagrams. The pH of precipitation of cobalt and nickel is very similar, even though Pourbaix diagrams show a pH gap of approx. two for the precipitation of both of these metals. [7] Pourbaix diagrams of cobalt, iron and nickel can be found in *Figure 1*.

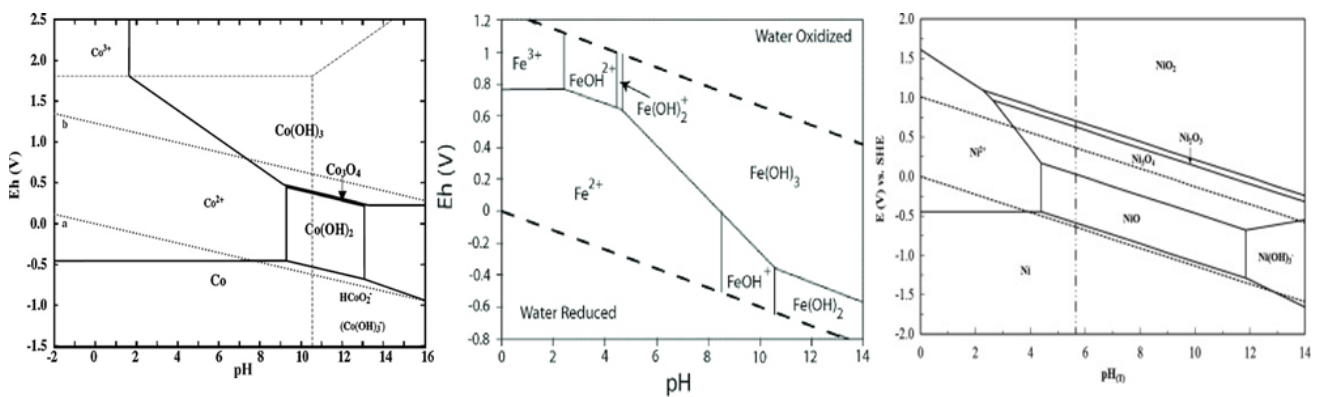


Figure 1: Pourbaix diagrams of cobalt, iron and nickel

Reasons for this can be metal complex interactions and/or shifted concentrations of the respected metal ions in comparison to Pourbaix, which can only be referenced if standard conditions are applied. A graphic overview of metal ion concentrations in a PLS of lateritic ore can be found in *Figure 2*.

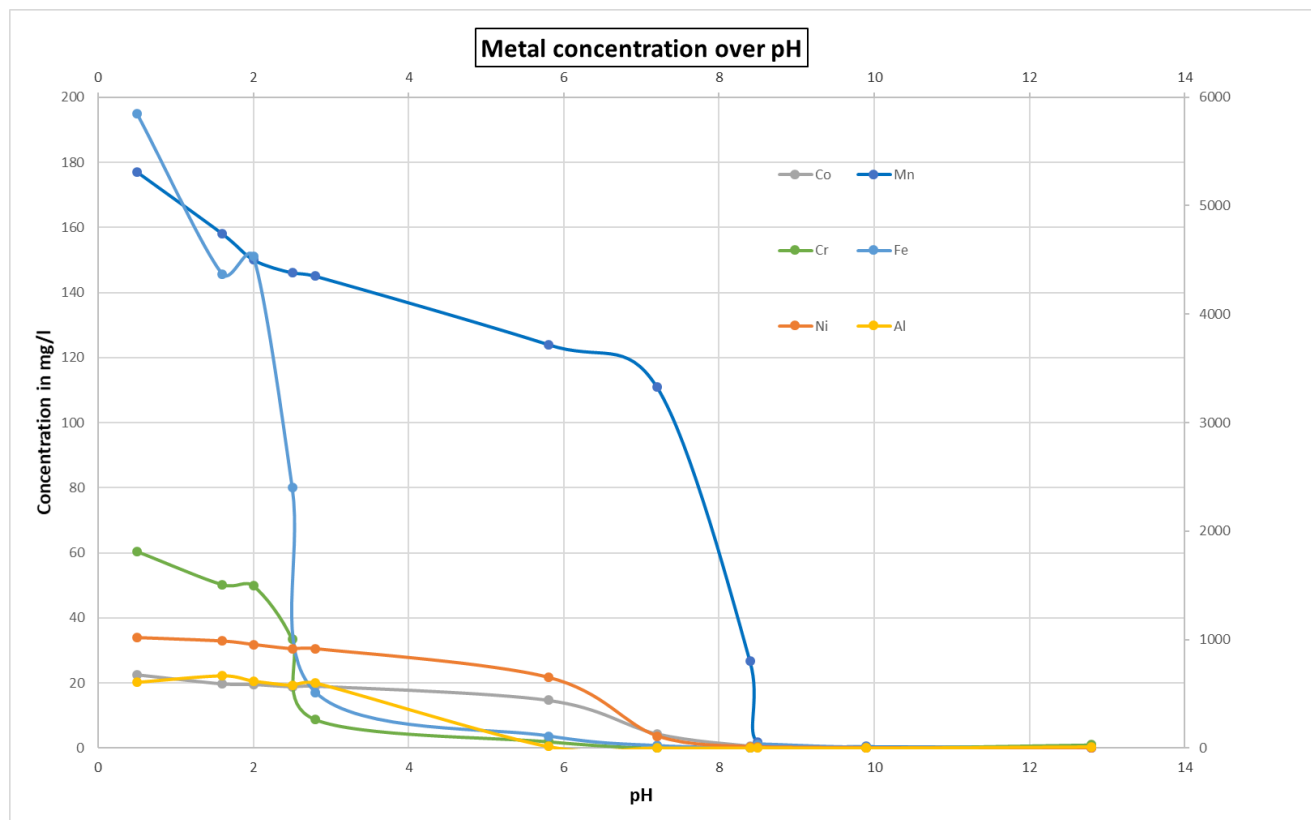


Figure 2: Metal concentration in PLS over pH

Analysis of the visible changes that can be observed during the trial lead to the conclusion that there are four characteristic pH points, at which metal precipitation of the main compounds take place. One being at pH 1.5, where most likely transition from Fe^{3+} to Fe^{2+} takes place. Major precipitation of Iron occurs at pH 3; at pH 4, over 95% of the Fe is removed. Chromium ions behave very similar to iron, as precipitation rate is alongside the one of aftermentioned. Aluminum as another main impurity precipitates at higher pH comparing to Fe, namely at 4. Nickel and Cobalt are removed from the solution at pH 5.5, with aftermentioned precipitating at slightly higher pH. Most critical element for the system is considered Manganese, as its precipitation is at higher pH than the ones of Nickel and Cobalt, making it hard to separate it from the PLS of both of the desired metals. Precipitation of different metal ions are summarized in the following **Table 4**.

Table 4: Precipitation of different metal ions in a PLS of lateritic ore

Element	pH of precipitation
Fe	3 - 4
Cr	2.5 - 4
Al	4 - 5
Ni	5.5 - 7
Co	6 - 7.5
Mn	7 - 9

Conclusion

Precipitation of different metals at characteristic pH values was obtained. This leads to the conclusion, that treatment with NaOH, adjusting the pH value, gives one a PLS consisting mainly of Cobalt, Nickel and Manganese. Precipitation behavior in the lateritic ore system is deviant to

Pourbaix diagrams of the respected metals. It is shown, that selective removal of undesired metal ions from a PLS of lateritic ore can be done. Further studies will be performed using measurements of redox potential in order to get a better understanding of the metal ion behavior inside of the PLS.

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