



# Ferric and Cupric Chloride Leaching of Valuable Metals from Process Residues

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**Keywords:** process residues, cyanide-free, gold leaching, valuable metals

## Abstract

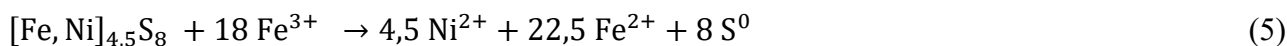
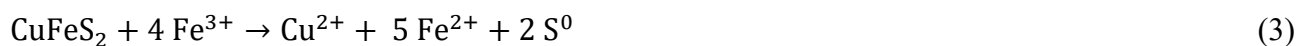
The object of the current study was to compare the extraction yields of various valuable metals from process residues by ferric and cupric chloride leaching as an alternative to cyanidation. Flotation tailings, with low amount of gold, copper, nickel, cobalt and zinc were used as a raw material. In the chloride leaching experiments, the effect of the oxidant type and concentration ( $[\text{Fe}^{3+}]$  and  $[\text{Cu}^{2+}]$  from 10 to 50 g/L), was investigated on the metals extraction. At the same time, pH (1 and 1.8), temperature (95 °C), solid/liquid ratio (25 %), oxygen feed rate (1200 mL/min), leaching time (24 h), and stirring rate (950 rpm) were kept constant. Additionally, the reference leaching experiment with sodium cyanide (NaCN) at 22 °C, pH = 11, solid/liquid ratio of 25 %, air feed rate 500 ml/min, stirring rate 400 rpm and 24 hours of leaching time was run to benchmark leaching efficiencies of cyanide-free processes. The results showed that the maximum gold extraction was observed with cyanidation (78 %) and followed by ferric and cupric chloride leaching. For copper, the extractions were higher in chloride leaching (75 – 100 %) whereas cyanide could dissolve 50 % of copper. Extraction of nickel and zinc were slightly higher in ferric chloride leaching compared to cupric chloride leaching, but cobalt extraction was similar in both chloride leaching methods. However, extraction of these metals was insignificant in cyanide leaching. With these results, it seems that chloride leaching with the presence of cupric and ferric oxidants can be used as an alternative cyanide-free method for extraction of metals from process residues.



# 1 Introduction

Significant amount of ores have been processed every year by the mining industry producing along concentrates tons of mine tailings, which carry low economic value. The value of tailings can potentially be recovered by new innovative recycling, reusing and re-engineering processes, thus contributing to circular economy. With constant push from the markets to produce metals and steadily depleting Earth's resources, there is an obvious necessity to unlock the potential of those residues. One example of potential group of industrial residues are flotation tailings, since a mine is usually focused on concentrating one or two metals in one concentrate. However, other metals present in the ore in lower grades, such as precious metals, are not frothed by flotation and may thus be left in tailings [1], [2].

Hydrometallurgical processes can provide the possibility to economically recover metals from low-grade ore bodies and process residues. Although cyanidation is the most used process to extract gold, the interest in cyanide-free processes has been increased due to the toxicity and low effectiveness of the former in the treatment of complex ores [3], [4]. With ability of high metal dissolution rate, chloride leaching in the presence of an external oxidant, such as cupric ions  $[\text{Cu}^{2+}]$  and ferric ions  $[\text{Fe}^{3+}]$  is one of the developing alternative process to recover precious and base metals from primary and secondary ores [5] – [8]. Also, the presence (or formation) of a stable complex between chloride and cuprous and cupric ions, low sulphate formation during the leaching process and keeping the elemental sulphur in the residue may in certain cases be considered as additional advantages of chloride leaching [9]. Seisko et al. [10] demonstrated that dissolution of gold into the chloride solution in presence of ferric ions requires an oxidation potential  $\geq 480$  mV (vs. Ag/AgCl), whereas in the presence of cupric ions it requires  $\geq 778$  mV (vs. Ag/AgCl). Ferric and cupric ions affect significantly the gold dissolution rate at high temperatures ( $\sim 95$  °C) and at low pH (1 – 1.8). Also, oxygen plays a very important role as an oxidant in chloride leaching to maintain the ratio of Fe(III) to Fe(II) and Cu(II) to Cu(I). Reaction 1 shows the gold dissolution reaction in ferric chloride leaching [11], [12]. Reactions 2 – 4 present how ferric reacts with all the components that raw material has. [13] – [15]. It need to be noted that these reactions are simplifications as in reality copper or iron species prevail mostly in complexed form [16], [17].



Aim of the study was to compare the efficiency of ferric chloride with the earlier published cupric chloride leaching [18] in the gold extraction from low grade flotation tailings. Additionally, conventional cyanide leaching was applied as a reference experiment. Also, the extraction of copper, nickel, cobalt and zinc were investigated.



## 2 Experimental

### 2.1 Material and analytical methods

Tailings from a flotation process were used as a raw material in this study. Chemical characterization of the material was performed by total leaching of the sample followed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; ThermoScientific iCAP 6000) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS; ThermoScientific iCAP Q). Mineral composition was defined by X-ray diffraction and Scanning Electron Microscope. Iron, copper, cobalt, nickel and zinc were found in the sample at 3.6 wt.-%, 0.09 wt.-%, 0.04 wt.-%, 0.03 wt.-% and 0.04 wt.-%, respectively. Gold was observed as free milling with grade of 0.2 ppm by fire assay. 83 % of the sample composed by hornblende-type amphibole, quartz, and dolomite minerals. Besides, phlogopite, chlorite, and magnetite were present as gangue minerals. Pyrrhotite (2.85 %), and pyrite (1.83 %), with accessory chalcopyrite (0.25 %), pentlandite (0.08 %), and sphalerite (0.07 %) were the most occurring sulphide minerals in the sample. Laser diffraction method was used for measuring the particle size of the material. Particle size ( $d_{80}$ ) of the as-received material was 150 microns, and it was further ground for 120 min to run the leaching experiments with a finer size raw material ( $d_{80} = 26$  micron).

### 2.2 Leaching Experiments

Ferric, cupric chloride and cyanide leaching experiments were operated with ground material in Outotec Research Center, Pori, Finland. The cupric chloride results were already published earlier, and the more detailed kinetic extraction curves were presented [18]. Chloride leaching was conducted in a 2 L titanium reactor, with constant parameters of NaCl (250 g/L), temperature (95 °C), oxygen purging (1200 mL/min), solids concentration (25 %), and stirring rate (950 rpm). Ferric ions ( $\text{Fe}^{3+}$ ) and cupric ions ( $\text{Cu}^{2+}$ ) were added from copper (II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ ) and ferric (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) until concentration between 10 to 50 g/L. During ferric chloride leaching, the pH was adjusted to 1 with concentrated hydrochloric acid (37 % HCl) to keep iron soluble, whereas in cupric chloride pH was adjusted to 1.8. Cyanide leaching was run in 1 L glass reactor with 2 g/L sodium cyanide (NaCN) concentration at pH = 11, solids concentration of 25 %, 500 ml/min of air purging, and 400 rpm of stirring rate at room temperature (22 °C). To calculate the extraction yields, samples were taken from reactor at 0, 1, 2, 4, 8, 12, 16 and 24 h. After the filtration process, leaching solution and final solid were subjected to analyse of the Fe, Cu, Ni, Co, and Zn by ICP-OES. To analyse the Au concentration, ICP-MS and fire assay were used.



### 3 Results and discussion

#### 3.1 Comparison of metal extraction in ferric chloride leaching vs. cupric chloride leaching

The effect of ferric concentration (10 / 30 / 50 g/L) was investigated as oxidant in chloride leaching. Figure 1 shows the effect of ferric concentration on gold extraction as well as compared to corresponding cupric chloride leaching results. In ferric chloride leaching, maximum extraction of gold (67 %) was observed in 30 g/L (0,54 M) ferric ion concentration, however when oxidant level increased up to 50 g/L (0.9 M), gold extraction decreased (ca. 30 %-units). Similarly, Seisko et al. [11] mentioned that gold dissolution increased when ferric concentration raised up to 0.5 M, however above this level it did not change considerably. This behaviour differs from the earlier published cupric chloride leaching results [18], where the authors showed that for the same level of oxidant concentration (30 g/L), 44 % of gold could be dissolved, but when the concentration of oxidant was increased further, the dissolution of gold increased up to 58 %. Also, at lower oxidant concentrations (10 g/L) of ferric chloride leaching resulted remarkably higher extraction (ca. 35 %-units) of Au compared to cupric leaching.

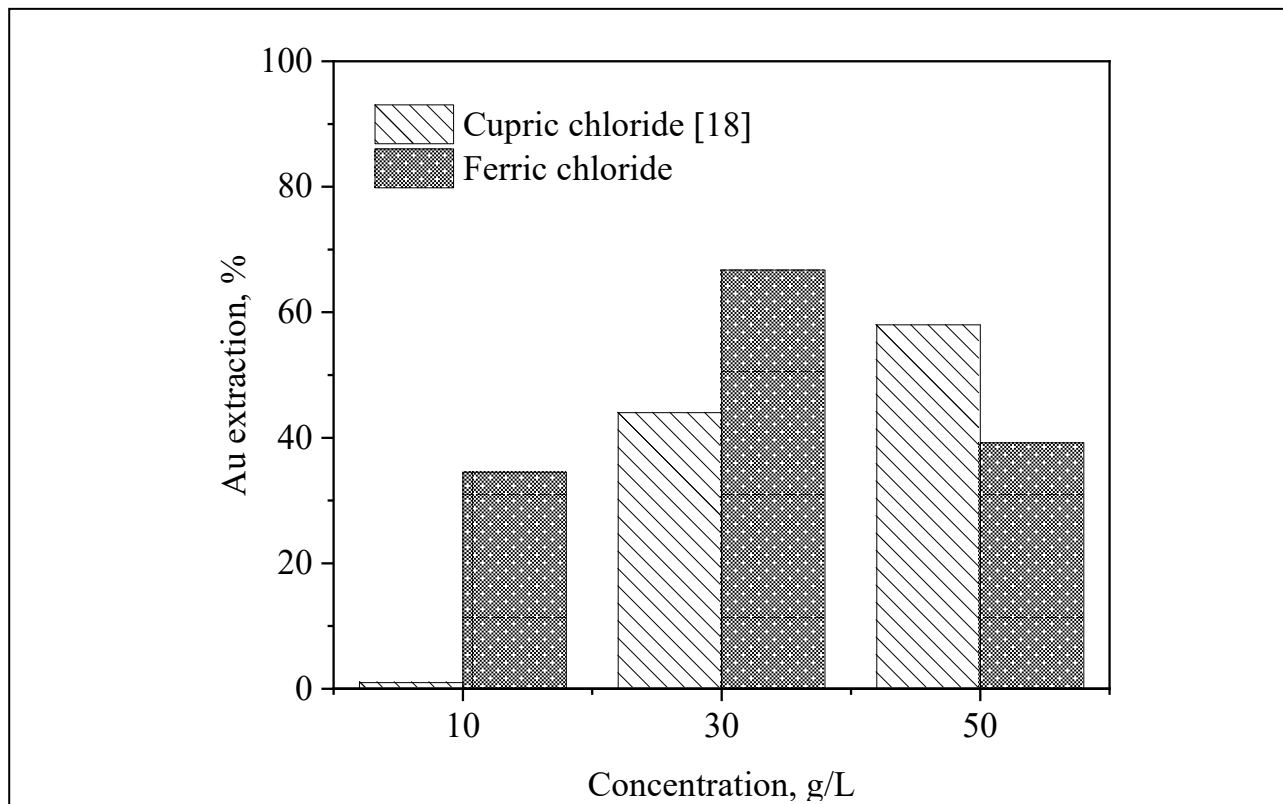


Figure 1: Extraction of gold in ferric and cupric chloride leaching at various oxidant concentration (pH = 1 – 1.8, T = 95 °C, concentration of NaCl = 250 g/L).

In ferric chloride leaching, maximum copper extraction (95 %) was obtained at the highest ferric ion concentration (50 g/L), however even with the lowest concentration of the oxidant (10 g/L), still 90 %



of copper could be extracted into the solution. On the contrary, dissolution of copper decreased when the oxidant concentration increased up to 50 g/L in cupric chloride leaching, and copper extraction was lower (15 – 30 %-units) than in ferric chloride leaching (Figure 2).

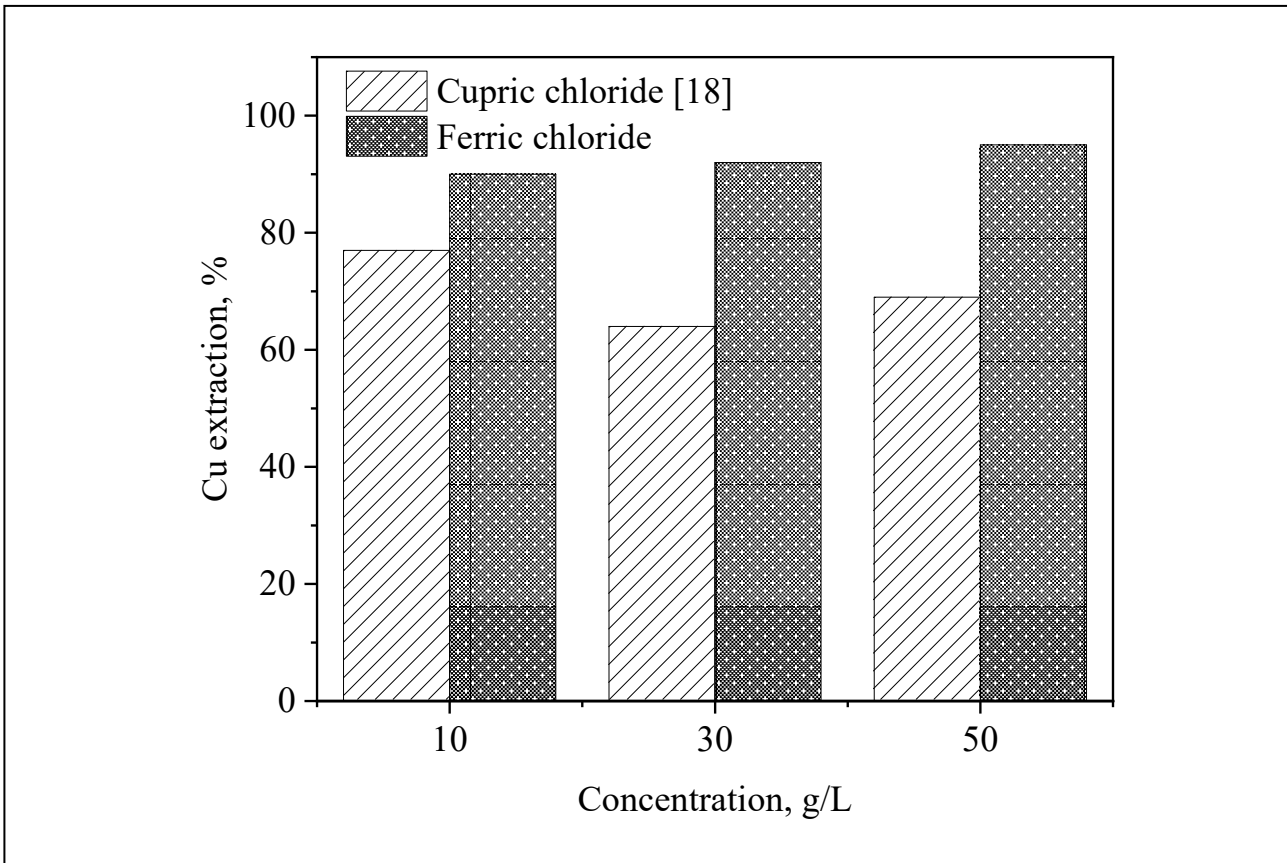


Figure 2: Extraction of copper in ferric and cupric chloride leaching with various concentrations of oxidants (pH = 1 – 1.8, T = 95 °C, concentration of NaCl = 250 g/L).

Extraction of cobalt, nickel and zinc into the chloride solution in presence of ferric and cupric ions as oxidant is demonstrated in Figure 3. Maximum extraction of cobalt, nickel, and zinc (67 %, 85 %, and 86 %, respectively) were obtained in ferric chloride leaching with 30 g/L ferric ions concentration and it was 10 – 20 %-units higher than in cupric chloride leaching. For ferric leaching experiments, dissolution of cobalt showed similar behaviour compared to cupric leaching with low dissolution rate. As mentioned in the previous study [18] that the low leaching kinetics of cobalt can be referred to cobalt is being with pyrite and chloride low influence on dissolution of pyrite. In all chloride leaching experiments, iron was remained in the leaching residues.

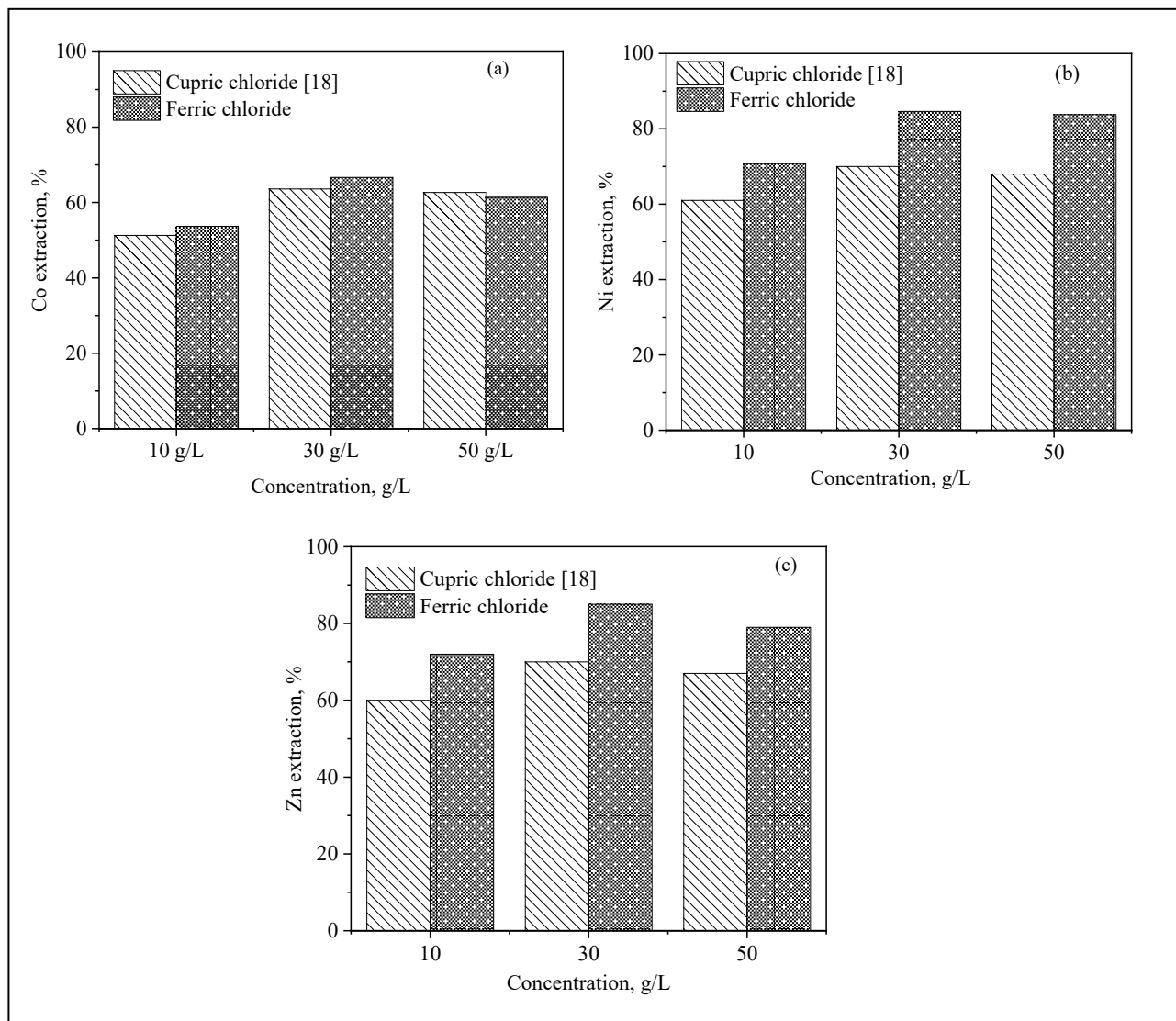


Figure 3: Extraction of cobalt (a), nickel (b) and zinc (c) in chloride leaching with various concentrations of oxidants (pH = 1 – 1.8, T = 95 °C, concentration of NaCl = 250 g/L).

### 3.2 Comparison of metal extraction in ferric chloride leaching vs. conventional cyanide media

Conventional cyanide leaching was investigated to compare the extraction of Au, Cu, Co, Ni and Zn in cyanide media vs. ferric and cupric chloride media with 30 g/L oxidant concentrations. The maximum dissolution of gold (78 %) was achieved in cyanide leaching, followed by ferric (67 %) and cupric (44 %) chloride leaching (Figure 4). However, extraction of copper in cyanide leaching was observed to be lower (54 %), compared to cupric and ferric chloride leaching where copper extractions were 15 and 35 %-units higher, respectively. There was also a significant difference between chloride and cyanide leaching in terms of the extraction of cobalt, nickel and zinc. In ferric and cupric



chloride leaching, dissolution of these metals reached up to 85 %, although in cyanide leaching, these metals mostly remained in the residue.

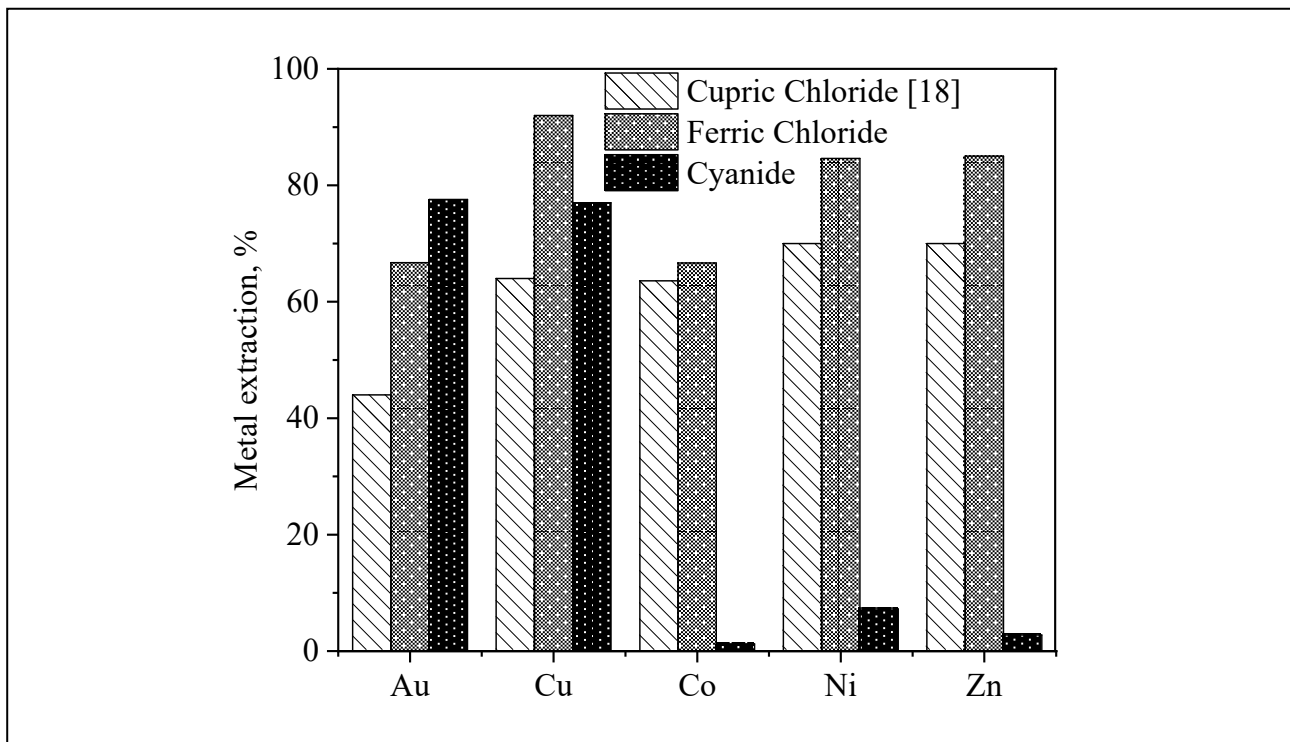


Figure 4: Comparison of metal extraction between cyanide and chloride leaching in presence of ferric and cupric ions.

## 4 Conclusions

This work shows the efficiency of ferric chloride leaching on the extraction of gold, copper, cobalt, nickel and zinc from low grade industrial process residues. Flotation tailings were used as a raw material, which contained iron, copper, cobalt, nickel, and zinc. In chloride leaching the investigated concentrations of ferric were 10 – 50 g/L in 250 g/L NaCl solution. Furthermore, conventional cyanide leaching was run as a benchmark test, where concentration of NaCN kept at 2 g/L.

The results indicated that in chloride leaching, the metal extraction efficiency for Au, Cu, Co, Ni and Zn was mostly higher with ferric ion as an oxidant compared to cupric ion. The only exception was cupric concentration of 50 g/L which could facilitate higher Au and Co yield. For base metals extraction, chloride leaching was shown to be much more effective than cyanide. This as a consequence of high pH (11) in cyanide leaching compared to low pH used in chloride media (1 – 1.8). However, cyanide had 10 %-units higher gold extraction compared to chloride media. These findings suggest that although the ferric leaching could not provide a superior leaching behaviour of gold, the non-toxic and environmental friendly chloride leaching method can be used as an alternative to cyanide leaching for efficient gold and base metal recovery from low-grade ores and industrial process residues.



## Acknowledgements

This research has received funding from the European Union's EU Framework Program for Research and Innovation Horizon 2020 under Grant Agreement No. 721385 (MSCA-ETN SOCRATES); project website: <https://etn-socrates.eu>. The authors would also like to thank Emil Aaltonen Foundation for their financial support. “*GoldTail*” (Grant 319691) funding by the Academy of Finland is also acknowledged.

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