

A Comparative Study of Metal Extraction from Spent Catalyst Using *Acidithiobacillus ferrooxidans*

Haragobinda Srichandan, Sradhanjali Singh, Dong Jin Kim, and Seoung-Won Lee

Abstract—The recovery of metal values and safe disposal of spent catalyst is gaining interest due to both its hazardous nature and increased regulation associated with disposal methods. Prior to the recovery of the valuable metals, removal of entrained deposits limit the diffusion of lixiviate resulting in low recovery of metals must be taken into consideration. Therefore, petroleum refinery spent catalyst was subjected to acetone washing and roasting at 500°C. The treated samples were investigated for metals bioleaching using *Acidithiobacillus ferrooxidans* in batch reactors and the leaching efficiencies were compared. It was found out that acetone washed spent catalysts results in better metal recovery compare to roasted spent. About 83% Ni, 20% Al, 50% Mo and 73% V were leached using the acetone washed spent catalyst. In both the cases, Ni, V and Mo was high compared to Al.

Keywords—Acetone wash, *At. ferrooxidans*, Bioleaching, Calcined, Metal recovery.

I. INTRODUCTION

REFINERY industries use huge quantity of metal catalysts in order to produce desirable products from its precursor. These catalysts constitute of different metals such as, Ni, V, Co, Mo, Fe etc. The metals in the catalyst are present in the form of metal ion, metal oxide and metal sulfide [1]. The catalysts used continuously until its catalytic value approaches zero during the process. These deactivated catalysts now considered as waste materials and referred as spent catalyst. Due to heavy metal content, spent catalyst categorized into hazardous waste. The spent catalyst need to be processed for the total metal recovery prior to its safe disposal. Pyro-metallurgical and hydrometallurgical techniques have been

used to recover metal values from spent catalyst [2]-[3]. However, both the processes are energy expensive and therefore have not been applied for a larger scale application. Recently, research focus has been shifted towards an alternative technique known as biohydro-metallurgical process.

Biohydro-metallurgical processes employed for recovery of metals are eco-friendly and cost effective. In the past, many studies have been reported by using iron and sulphur-oxidizing microorganisms [4]-[7]. Briand et. al. uses *Acidithiobacillus thiooxidans* to treat a spent vanadium-phosphorous catalyst [8]. Mulak et al. have studied the effect of different parameters on the rate of nickel leaching from spent nickel oxide catalyst (NiO and Al₂O₃) [9].

The leaching of metals from ores or solid waste using bacteria depends upon the bacterial oxidation of Fe²⁺ and sulfur into Fe³⁺ and H₂SO₄, respectively. The metal bioleaching by fungi depends upon the production of organic acids such as citric acid, oxalic acid etc. Use of heterotrophs (fungi) is difficult for scale up process as it requires sterile environment for operation which makes the process expensive. Nevertheless, many investigations are performed for metal recovery from petroleum refinery spent catalyst using Fe/S oxidizing bacteria. Notably, these experiments were conducted for longer duration and performed in shake flasks. Therefore, further scales up studies are needed to confirm the leaching potentiality [10]-[11].

In the present study, an effort was made to conduct the experiments in 2.5L batch bioreactor using Fe/S oxidizing *Acidithiobacillus ferrooxidans* for leaching the metals from spent catalyst.

II. MATERIALS AND METHODS

A. Spent Petroleum Catalyst

The spent catalyst used for bioleaching experiments was received in bulk from the Petroleum Refinery Company located in South Korea. The raw spent catalyst was coated with oily matter and was subjected to acetone washing in a soxhlet apparatus followed by drying in a hot air oven. Roasting of the raw spent catalyst was carried out in a crucible by taking 100g of air dried sample and roasted in atmospheric oxygen flow in a temperature controlled (10°C/ min) muffle furnace for 3h. muffle furnace. The dried acetone washed and roasted spent catalysts were ground separately using ring mill. The particle size distribution was determined by using

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Malvern Mastersizer (Malvern Instrument). The particle size distribution was normal for all size fractions ranging from 0.020 to 2000µm.

Thermo-gravimetric analyses were carried out using a TG/DTA analyzer (SHIMADZU) with air as carrier gas. The sulphur and carbon analysis was done by a LECO CS -600 analyzer. Quantitative evaluation of minerals presents in the feed and treated samples were analyzed by mineral liberation analyzer (MLA, MLA650F, FEI, US) (Figure is not shown here). FESEM images of raw, acetone and roasted spent catalyst was done and shown in Fig. 1.

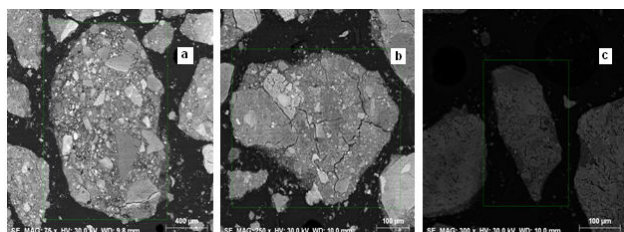


Fig. 1 FESEM images of raw, acetone washed and roasted spent catalyst

The chemical composition of the acetone washed and calcined spent catalyst was determined by Induced Couple Plasma Spectroscopy (OES) (PerkinElmer's Optima 8000) for elements such as Ni, Al, Mo, V, Fe and S. The chemical content for acetone washed and roasted spent catalyst is presented in Table I. For the identification of the mineral phases, mineralogical analysis was carried out by powder X-ray diffraction (Smartlab, Rigaku, Japan). The mineral phases found in the feed spent catalyst were shown in Table II.

TABLE I
CHEMICAL ANALYSIS OF ACETONE WASH AND ROASTED SPENT CATALYST FEED

Description	Elemental Composition (%)				
	Ni	Al	Mo	V	Fe
Acetone Washed	3.31	20.56	2.58	11.4	0.21
Roasted	3.97	22.6	2.82	14.3	1.1

TABLE II
MINERALOGICAL PHASES OF SPENT CATALYST FEED

Minerals
Iron aluminum sulfide
Nickel vanadium oxide
Vanadium phosphorus sulfide
Molybdenum vanadium oxide
Aluminum oxide
Vanadium oxide
Molybdenum oxide
Nickel aluminum oxide
Aluminum vanadium oxide
Iron Molybdenum oxide
Nickel sulfide hydrate

B. Microorganism and Growth Condition

Pure strain of *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*), was obtained from the Korea Research Institute of Bioscience and Biotechnology (KRIBB) culture center. The bacterium was grown in IEM medium composed of three components solution A, B and C. Solution A, is prepared by

dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.78 g) in 1L of distilled water acidified with concentrated H_2SO_4 to *ca.* pH 1.8, the final pH was adjusted to 1.5 after the salt dissolved. This solution was stored at 5°C. Solution B consists of macronutrients nutrients composed of $(\text{NH}_4)_2\text{SO}_4$ (5.00g), K_2HPO_4 (2.50g), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (2.50g), and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.100g) dissolved in 1.00L of distilled water and adjusted to pH 1.50 ± 0.05 with concentrated H_2SO_4 . Solution C consists of micronutrients solution composed of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (2.49g), $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ (2.81g), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (1.69g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (1.77g), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (2.62g) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (2.87g) dissolved in 1.00L of distilled water and adjusted to pH 1.50 ± 0.05 with concentrated H_2SO_4 . Medium for batch cultures is prepared by adding to distilled water acidified with H_2SO_4 : ferrous sulfate heptahydrate solution A (1.0mLL^{-1}); macronutrient solution B (20mLL^{-1}); and micronutrient solution C (1.0mLL^{-1}) [12]. The final pH was adjusted to 1.68 ± 2 . After achieving complete growth, the bacterial cells were passed through a membrane filter ($0.45\mu\text{m}$) and the cells were inoculated in respective batch reactors for further experimentation.

C. Bioleaching Experiments

Experiments were carried out in stirred tank batch reactors (2.5L) using *At. ferrooxidans*. All the experiments were performed in a controlled environmental condition such as pH 1.4 ± 0.05 , stirring speed 250rpm, working volume 1L. Prior to the addition of spent catalysts, the bacterial cells were suspended in fresh IEM medium supplemented with 4g/L Fe^{2+} ($20\text{g/L FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 1% elemental S^0 at pH 1.69. When all Fe^{2+} was oxidized to Fe^{3+} and the pH of the medium reached to 1.4, acetone washed and roasted spent catalysts were added at 1% (w/v) pulp density (10g/L) respectively into the reactors and experiments were conducted as per the aforesaid experimental conditions mentioned previously. Two control set experiments were also performed without addition of bacterial cells under same conditions. To the above reactors, continuous air was supplied at a flow rate of 1 l/min to ensure homogenous mixing of the bioleaching pulp.

Sampling was done at regular intervals for analysis of Fe, Ni, Al, Mo, V. The viable microbial planktonic cell count was carried out using improved Neubauer counting chamber under a phase-contrast microscope (Olympus Model No BX51TF). pH measurements were conducted using an Orion portable pH meter whereas the redox potential was measured using a platinum electrode with a Ag/AgCl reference electrode. Sulphate analysis was carried out by using barium chloride precipitation method at 420nm. Fe^{2+} estimation was performed using 1,10-phenanthroline-spectrophotometry method at 520nm. All the experiments were performed till 100 hrs and after that it was terminated and the bioleach liquor was allowed to pass through Whatman filter paper No. 1 for separating liquid and solid. The solution was sent for ICP-OES analysis after dilutions. The leaching yield of the desired element was calculated based on both the elemental content of the feed and leach liquor as per the formula given:

$$\text{Leaching yield (\%)} = \left[\frac{M(r)}{M(f)} \right] \times 100$$

where, M(r) is the metal (Ni, V, Mo, Al) content in the leach liquor and M(f) is the metal (Ni, V, Mo, Al) content in the feed.

III. RESULTS AND DISCUSSION

A. Characterization of Spent Catalyst

The high levels of C and S present in the spent catalyst, decreased with rise in roasting temperature and effectively removed at around 500°C. Maximum weight loss observed was 16% at 600°C. As the roasting temperature increased, the particle size increased most likely due to sintering of the particles occurring at elevated temperatures. TG/DTA profile of the raw, acetone and roasted spent catalyst are illustrated in Fig. 2. The temperature difference i.e. the peaks in the DTA plot are associated with phase transitions or thermal events such as desorption, combustion etc. The plot for the raw catalyst is more complex than for the acetone washed sample. From ambient temp there is a very slight cooling associated with loss of volatile hydrocarbons, as the temperature increases, the DTA plot has a peak at approx. 285°C, likely due to oxidation of hydrocarbons. Note that this peak is very small for the acetone washed sample, as the temperature increases further the DTA plot has another peak at app. 364°C likely due to the oxidation of the carbonaceous material, this peak also occurs in the acetone washed sample at app. 374°C. It is to be noted that the two oxidation peaks for the raw catalyst overlap. The XRD spectrum of unroasted spent catalyst was fairly similar to those of γ -Al₂O₃ support. Moreover, for roasted sample, along with the existing peaks some new peaks corresponding to 2 θ values 40.62 and 53.38 were developed. This can be attributed to the mixed oxide formation of these metals.

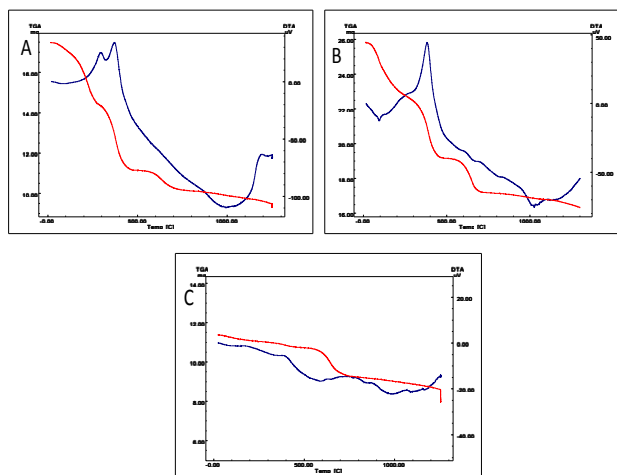
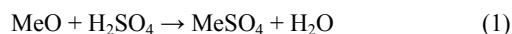


Fig. 2 TG/DTA curve for (A) acetone washed, (B) roasted and (C) raw spent catalyst

A. Change in pH

All the experiments were conducted under controlled pH condition (pH 1.4±0.05). Fig. 3 represents the change in pH profile during the experimentation. Initially, rise in pH was

observed in all the cases. After 15 hrs, no such rise in pH was observed and becomes more or less constant. It reaches 1.9-2.2 by the end of 100hrs for control set experiments. Whereas, very less rise in pH value was observed with bioleaching experiments (pH 1.6) compared to control experiments (1.9-2.2) within 15hrs of the experimentation. It was due to the potentiality of the microorganism to produce acid at regular intervals which was not possible in control set experiments. As the bioleaching process continues, slight decrease in pH value was observed and after that no such difference in pH value was monitored. The initial increase in pH for all the experiments can be explained due to the acid consumption by the metal oxides present in the spent catalyst. The dissolution of the metal oxides in the spent catalyst is usually an acid consuming process and can be represented as per (1):



where Me represents the metal such as Ni, Al, Mo, V, Fe etc.

The difference of the pH value can be explained by the activity of bacteria. *At. ferrooxidans* has the ability to oxidize elemental sulfur into H₂SO₄ which results in decrease in pH. The acid produced by the bacteria compensated the acid consumed by metal oxides during bioleaching experiments. On the other hand, in the blank experiments, the acid consumed by spent catalyst was not compensated due to the absence of bacterial activity resulting in high pH.

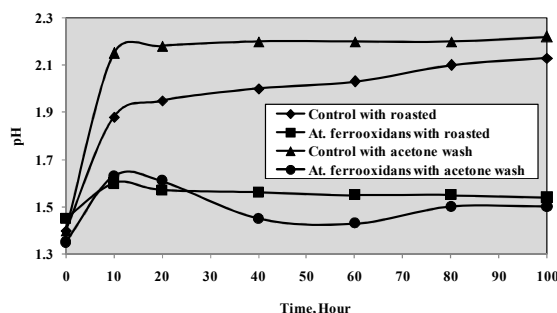
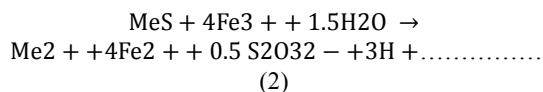
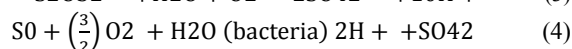
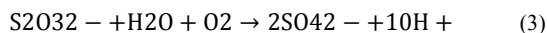


Fig. 3 The pH evolution profile of roasted and acetone washed spent catalyst

Spent catalyst was found to contain most of the metals in oxide form as shown in Table I. Some of the metals were also present in sulfidic form. The metal sulfides can be categorized into two types, acid soluble and acid insoluble. The acid insoluble metal sulfides followed the thiosulphate pathway as in the case of pyrite (FeS₂) and molybdenite (MoS₂) whereas acid soluble sulfides follow the polysulphide pathway [13]. It can be assumed that spent catalyst also followed the thiosulphate pathway. The spent catalyst contains iron and molybdenum sulfides which are oxidized by the Fe³⁺ ion generated by the bacteria as shown in (2):



The sulphur intermediates formed ($S_2O_3^{2-}$ or S^0) is oxidized by the bacterium to form sulphate ions and H^+ ions compensating the part of acid consumption (3) and (4).



The protons and ferric ions produced during oxidation by the bacteria keep the pH quite low enough for metal solubilization.

C. Effect on Redox Potential

Fig. 4 shows the redox potential profile for all the experiments. The redox potential decreases initially suggesting that the metals leached into solution from the spent catalyst remained stable in the reduced state. The redox potential for two control experiments follows similar trend whereas for acetone wash spent catalyst a slight decrease in the redox value was observed (560mV) compared to the roasted spent catalyst (580mV). Fig. 5 represents the effect of Fe^{2+} concentration on redox potential for bioleaching experiments. In the case of acetone washed spent catalyst, the Fe^{3+} iron is reduced to Fe^{2+} iron as a result of metal leaching from spent catalyst. This causes increase in Fe^{2+} concentration (150mgL^{-1} to 1335mgL^{-1}) and decrease in the redox potential from 580mV to 515mV within first 20hrs.

However, after that decrease in the Fe^{2+} concentration was observed due to the conversion of Fe^{2+} to Fe^{3+} by the bacteria which in turn increases the redox potential till 55hrs. The generated Fe^{3+} further reduced by spent catalyst causing a decrease in redox potential till the end of the experimentation and reaches to 505mV.

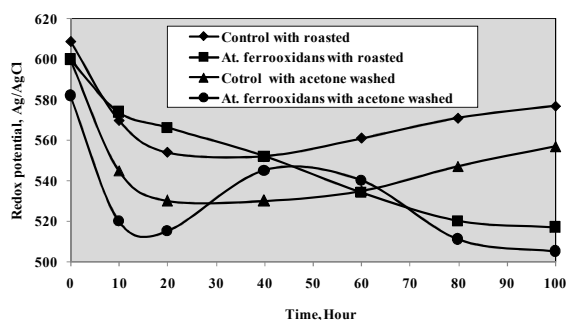


Fig. 4 Plot showing redox potential profile roasted and acetone washed spent

However, in roasted spent catalyst, the Fe^{2+} concentration gradually increase from 45mgL^{-1} to 1400mgL^{-1} . This led to decrease in redox potential from 620mV to 516mV till the end of experiment.

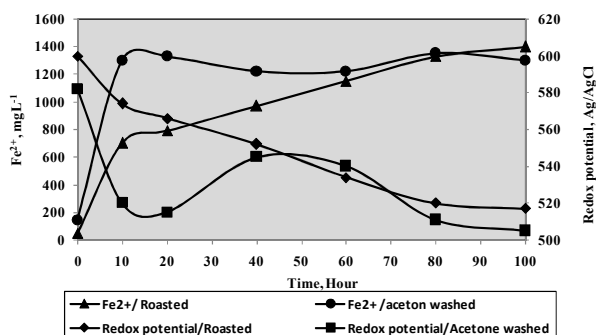


Fig. 5 Change in Redox potential and Fe^{2+} during bioleaching of roasted and acetone washed spent catalyst

D. Bioleaching Yield

Fig. 6 represents the leaching profile of metals in the control and in bioleaching experiments. As can be seen from the Fig. 6 the leaching of Al was very slow and only 20% Al was leached out from control and bioleaching experiment whereas, Ni, Mo and V was comparative faster.

In the bioleaching experiment, higher recovery was Mo (56%) and V (54%) was achieved compared to the control experiment (43% Mo and 34% V). Ni leaching was found to be 46% in control and 50% in case of bioleaching experiment. For acetone washed spent catalyst, 20% of Al leaching was extracted in both the cases (Fig. 6). However, in bioleaching experiment, high leaching yield of Ni (83%) and V (73%) was observed compared to the control (50% Ni and 40% V). The results indicate that Al and Mo leaching yield was almost the same in bioleaching and control. In the case of V, bioleaching resulted in higher yield compared to the control.

Among all the experiments, bioleaching with acetone washed spent catalyst resulted in high metal recovery. At the end of bioleaching experiment, around 83% Ni, 20% Al, 50% Mo and 73% V were recovered from the acetone washed spent catalyst.

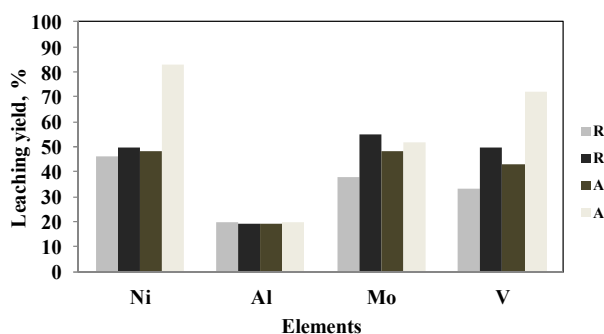


Fig. 6 Histogram showing metal recovery for acetone washed, roasted and control spent catalyst

IV. CONCLUSION

The present investigation deals with the bioleaching of spent petroleum catalyst using Fe^{2+}/S^0 oxidizing *At. ferrooxidans*. The spent catalyst used in the present study was pretreated with acetone and roasting. Bioleaching experiments

were separately conducted with acetone washed and roasted spent catalyst. *At. ferrooxidans* was found to be effective in producing Fe^{3+} and acid in presence of acetone washed spent catalyst while only acid in presence of roasted spent catalyst. The leaching yields of Ni, V and Mo were significantly high compared to the Al. The metals yields for all the experiments were as follows: Ni (50-83%), Al (19-20%), Mo (43-62%) and V (34-73%). Among all the experiments, bioleaching using acetone washed spent catalyst resulted in highest recovery of metals (83% Ni, 20% Al, 50% Mo and 73% V). The higher leaching yield with acetone washed catalyst might be due to the generation of acid as well as Fe^{3+} by *At.ferrooxidans*.

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REFERENCES

- [1] M. Marafi, A. Stanislaus, "Optios and process for spent catalyst handling and utilization" J. Hazard. Mater. Vol. 101, p.123-132, 2003.
- [2] M. Marafi, A. Stanislaus, "Spent catalyst waste management: A review Part I-Developments in hydroprocessing catalyst waste reduction and use" Conserv. Recycling. Vol. 52,, p.859-873, 2008.
- [3] D. Pradhan, D. Mishra, D. J. Kim, J.G. Ahn, G.R. Chaudhury, "Bioleaching kinetics and multivariate analysis of spent petroleum catalyst dissolution using two acidophiles" Journal of Hazardous Materials. Vol.175, p. 267-273, 2010.
- [4] R. M. Gholami, S. M. Borghei, S. M. Mousavi, "Bacterial leaching of a spent Mo-Co-Ni refinery catalyst using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*" Hydrometallurgy. Vol.106, p.26-31, 2011.
- [5] D. Pradhan, D. J. Kim, J. G. Ahn, G. R. Chaudhury, S. W. Lee, "Kinetics and statistical behavior of metals dissolution from spent petroleum catalyst using acidophilic iron oxidizing bacteria" Journal of Industrial and Engineering Chemistry. Vol.16, p.866-871, 2010.
- [6] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, Y. H. Rhee, "Bioleaching of spent hydro-processing catalyst using acidophilic bacteria and its kinetics aspect" J. Hazard. Mat. Vol.152, p.1082-1091, 2008.
- [7] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, Y. H. Rhee, "Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs" Hydrometallurgy. Vol. 88, p.202-209, 2007.
- [8] L. Briand, H. Thomas, E. Donati, "Vanadium (V) reduction in Thiobacillus thiooxidans cultures on elemental sulfur" Biotechnology letters. Vol. 18, p. 505-508, 1996.
- [9] W. Mulak, B. Miazga, A. Szymczycha, "Kinetics of nickel leaching from spent catalyst in sulphuric acid solution" Int. J. Miner. Process. Vol. 77, p.231-235, 2005.
- [10] D. Mishra, D. J. Kim, D. E. Ralph, J. G. Ahn, Y. H. Rhee "Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs" Hydrometallurgy. Vol. 88, p. 202-209, 2007.
- [11] D. Mishra, J. G. Ahn, D. J. Kim, G. R. Chaudhury, D. E. Ralph, Dissolution kinetics of spent petroleum catalyst using sulfur oxidizing acidophilic microorganisms. Journal of Hazardous Materials. Vol. 167, p.1231-1236, 2009.
- [12] Blight, K.R., Ralph, D.E., 2004. Effect of ionic strength on iron oxidation with batch cultures of chemolithotrophic bacteria. Hydrometallurgy 73, 325- 334.
- [13] T. Rohwerder, T. Gehrke, K. Kinzler, W. Sand, "Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation" Appl Microbial Biotechnol. Vol 63, p. 239-248, 2003.