

REVIEW ARTICLE

New Trend of Leaching of Silicate and sulfide Minerals

By Dr. Tarek Abdel Wahab Ali El Barbary

Chemical and Electrochemical Department Minerals Technology Division Central Metallurgical Research & Development Institute (CMRDI)





Contents

New Trend of Leaching of Silicate and sulfide Minerals Error! Bookm	ark not defined.
Abstract	29
1. Introduction	29
1. Ore and Occurrence	29
1.1. Sulfides	29
1.1.1. Sulfide ore in Egypt	29
1.2. Silicate Ore in Egypt	28
2. Leaching processes	28
2.1. Leaching of sulfides	28
2.2. Mechanical Chemical activation of Sulfides	28
2.3. Pressure Leaching of sulfides	28
2.4. Bioleaching of Sulfides	28
3. Silicates	28
3.1. Leaching of silicate	28
3.2. Bioleaching of Silicate	28
Conclusion	29
References	29



New Trend of Leaching of Silicate and Sulfide Minerals

Dr. Tarek Abdel Wahab Ali El Barbary

Chemical and Electrochemical Department, Minerals Technology Division, Central Metallurgical Research & Development Institute (CMRDI)

Abstract --Although ore processing is an old technique, it is the technique that used to treat sulfide or silicate ores, a traditional and prevalent technique. Silicate ores as kaoline, clay, feldspare, nepheline syanite, silica sand, quartz, talc and zircon are treated with thermal melt. While sulfide ore as chalcopyrite, pyrite treated with thermal melt. But now a day facing challenge through new mineral hydrotherapy processes.

I. INTRODUCTION

The role of science and technology in economic development is continuously increasing. New trends in material science including mineral processing focused on economization of the existing technologies as well as the development of cost effective and energy saving techniques. Therefore, much emphasis is given to decrease both energy consumption and wastes. In addition, new technologies are being developed to maximize the utilization of industrial wastes for production of high value added products, microorganisms acquire great attention in material and mineral processing during the last few decades. Bioprocessing techniques do not require high temperatures or special material of construction which consequently decrease enormously both investment and running costs.

Moreover, these techniques are simple environmentally friendly and do not require sophisticated machinery. The present article processing of complex sulfide and silicate ores which are conventionally processed by energy intensive and multistage techniques in addition to its negative impact on the environment.

The proposed technique used for processing of complex sulfide and silicate ore depends mainly on the treatment of ores, even low grade by oxidizing or reducing bacteria.

To obtain valuable metals from ores as sulfides and silicates there are different technique required. Physical, physic-chemical and mechanical used in mineral processing. Chemical processing as extractive metallurgy which divided to hydro- and pyrometallurgy. Electrometallurgy is the most recent technology and came into existence only after the exploring of the large-scale electrical generator in the mid nineteenth century. Hydrometallurgy is discovered from four hundred years, while pyrometallurgy is the oldest technology. [1]

1. Ore and Occurrence

The ore is presence of rock or precipitation that contain sufficient minerals or sediment with economically important elements typically metals, that can be economically obtained from the deposit.[2] The ore are obtained from the earth through mining. They are dressed to obtain the valuable element or elements.

The nature of ore, mineral, concentrate, grade, form and presence will be affected on the cost and ore mining.

The economist of extraction must be compared with the metal price found in the rock to evaluate what ore can be explored, and which ore is low grade to be error to mining metal generally. Sulfide, silicate or native metals as native copper that are not dressed or concentrated in the earth's crust or noble metals not usually reacts with another element to form compounds such as gold.

To extract elements of interest from the processed ore or rock that contain minerals it must be extracted. Variety of geological processes from ore skulls. Ore formation process named as ore genesis.

1.1. Sulfides

The class of minerals that contain S^{-2} as major anoin named as sulfide mninerals. Some of those minerals are important because it contains a precious metals as gold or silver.

The sulfide class also contains other valuable elements as selenides teleurides antimonites bismuthinites and the sulfosalts[3]. Sulfide minerals are inorganic compounds.

1.1.1. Sulfide ore in Egypt

Sulfide mineralization is the main source for mining the elements, lead, zinc and copper in Egypt. The mineral is divided into four main types:

The first type named seposite which contain Lead and zinc sulfides

The second type contains copper or nickel with cobalt which present in AbuSwayel in South Eastern Desert



The third type contain copper – nickel sulfide deposits. This type of mineralization occurs in Layered maficultramafic instructions like gabbro Akarem and El Geniene and the fourth type are zinc, copper lead deposits this type minerlization is represented by group of small lenses associated with talc deposits in South Eastern Desert at Um Samuki, Helgit, Maakal Atshan, Darhib, Abu Gurdi, and Egat [4]. Some examples of sulfide ores are indicated in Figure 1.



1.2. Silicate Ore in Egypt

Silicate minerals in Egypt are divided to about 7 types. Silicate mineral contains mainly SiO₂ which represents 90% of earth crust.[5-7]



Figure 2: Photos of some silicate ores

A- Kaoline

Kaoline found in Egypt in three main localities, Sinai, along the red sea Coast and Wadi Kalabsha near Aswan. The estimated reserves in Sinai about 100 million tons, [8-10] most of Sinai Kaoline used in ceramic and saintering industries.

B- Clays

Clay reserves are located in Abu-Elrish Qibli and Bahari, Gebel Kubaney, Elakba El Saghera in Aswan[11].

C- Feldspare

Two types of feldspare are found in Egypt. Potash feldspare which known as pegmatite and the second is sodic, which known as albite the first one present in the Eastern Desert while the second found South Sinai.[12&13]

D- Nepheline Syanite

Nephelene Syanite present in Southern sector of the Eastern Desert, south Idfu Marsa Alam Road[14&15].



E- Sand Stone

It is maily contain silicon dioxide in crystalline form and contain also lime stone it is found in most of the mountain in Egypt. The high grade of silica that used in glass tableware are present as deposit of Wadi El-Daklil, The Eastern Desert. [16-18]. Some examples of silicate ores are indicated in Figure 2.

F- Talc

Talc present in different localities in middle and south of the Eastern Desert.[19&20]

G-Zircon

Reserves in Egypt are present along the medetraanian sea specially in the region between Rosetta and Domeiata on the sea coast[21].

II. LEACHING PROCESSES

Leaching is removal of valuable elements by dissolving them away from solids. Figure 3. Indicate the reactor of leaching.



Figure 3: Leaching reactor

A primary dissolving process in Hydrometallurgical operation, metal transferred from the mineral to aqueous solutions. In fact, there is selective dissolution of the valuable metal from the ore, concentrate or matte by the interaction with the active chemical solution. Because the dissolution is selective so most of the impurities not dissolves.[22] After leaching process the metal was separated from the solution. The solution of filtration named pregnant solution or leach liquor. The solid product is known as residue or tailings. It is important to find contain waste with low dissolution ability in order to have an acceptable separation of valuable metals.

Silver sulfide leached by cupric or cupreous substitution mechanism in copper – ammoniathiosulfate solution. Themodynamic equations indicate that the system of cuprus reaction is less favorable; although a big number of experiments in the literature indicate that the reaction proceed slowly.

Mixed ammonium thiosulfate complexes could lower the thermodynamic barrier to leaching so the presence of ammonium is necessary to accelerate the reaction. Although structure similarity between cupreous and silver phases it was found that the cupreous reaction was preferred. The cuprictetraamine reaction has been known to occur more rapidly in a solution.

Cupric-tetraamine complex is stable in solution give the maximum leaching rate of silver sulfide. A concentration of 50 and 100 mM studied to be under pure diffusion control (Briones and Lapidus, Trejo-Gallardo and Lapidus) as copper – ammonia – thiosulfate leaching system.

For copper concentration 2 order magnitude larger that the copper concentration of 1 mM there is a linear effect on leaching rate.

The very low concentration of the copper suggested under the chemical diffusion control. The chemical control may be results driving force associated with these conditions. The study of low concentration of copper needs more efforts [23&24].

Silver dissolution, each to the maximum dissolution when cupric in solution is fully complexes with ammonia with large amount of thiosulfate to increase the velocity of chemical step at the surface. Increase the addition of ammonia or increase pH decrease the cupric complex and Silver sulfide leaching rate.

Rising temperature has little effect on the leaching, but affect on more loss of ammonia. The application of these results on silver sulfide ore will demonstrated in the second part of this paper [25].

2.1. Leaching of sulfides

Jared and David use three complexes Ferric – EDTA ,Ferric – Oxalic and Ferric – Citric was tested as potential candidates for silver sulfide extraction using a rotating disk. For the three complexes there is no any precipitation of iron observed during the extraction.



Kinetically these three complexes were observed slow. The Ferric – EDTA show the best complex for the commercial implementation. Ferric – citrate is the slowest one for silver sulfide leaching and used low pH, which is not described for long termthosulfate stability.

After 1 day of leaching it was found that Ferric-EDTA is more prefreble for leaching where it dissolve about 70% of silver sulfide with loss 2.5 % of thiosulfate, while Ferric citrate loss 14% of the cupric ammonia thiosulfate system.

Although thiosulfate is low extraction results of gold, but still preferable. Extraction by 1% Hg up to 50% Hg, although it gives more recovery, but the environmental risks and high cost with the mercury contaminant still present.

The low leaching results of silver by thiosulfate is explained due to the mineralogical form at the condition tested. This illustrate the low recovery of silver by thiosulfate compared with cyanide. This work may be useful in the future. The recovery of silver by cupric – ammonia thiosulfate is able in an aerobic aor anaerobic invironment in presence or absence of EDTA.

In aerobic environment the acceleration of leaching and decrease the thiosulfate consumption. In anaerobic environment the leaching is slow and the consumption of thiosulfate is very low theses conditions are suitable to heap leaching. It is a challenge of the system that the ability of leaching small amount of copper, the availability of copper in solution for silver leaching.

Jared and David study the most suitable ferric complex for silver sulfide leaching. Ferric-oxalate is precipitate due to the nature of the ore so it is ineffective. It was found that Ferric – citrate is more consuming of thiosulfate that Ferric – EDTA due to the low pH of the solution. Generally it must be more study about the reactivity of those complexes toward the components in ores.[26]

The metal recovery from the copper sulfide tailing depending on the mineral structure of the ore. In copper sulfide mineral with the composition of 31.5, 38.85 and 15.06 of pyrite, silicate and quartz minerals respectively. Tao and Chen can extract the elements Cu, Zn, Mn and Fe with the percentage 98.45%, 21.41%, 56.13 1nd 17.25 respectively by fractional precipitation. In order to increase the leaching they treat the sludge by using sulfuric acid at the ambient pressure. 0.24 ml/g of H₂SO₄, S:L of 1:2, stirring velocity 400 RPM, and the extraction time reach in 2 hours.

The leaching of the elements from the sludge Cu, Zn, Mn, and Fe reach to 19.53%, 33.48%, 14.10% and 49.13% respectively.[26]

After treatment of the tailing of copper from filtrate reach of 95.45%, 93.74%, 89.70 and 93.29 for the metals Fe, Cu, Zn and Mn respectively . While the previous elements can extract from the sludge with 49.13%, 19.53%, 33.48% and 14.10 for the previous metals.[27]

Mari et al study the leaching of four different chalcopyrite samples from different mined around the world of copper sulfide dissolved in concentrated copper chloride. They found that the four samples iron and copper precipitated with different ratios not with equal ratios as expected.She also found that the burgling oxygen leads to precipitation of covelite. Extraction of bornite not effect on the acidity and there are no strong copper precipitation.[28]

Pretreatment of by oxidative ammoniacal solution studied by Feng and Van Deventer the overall leaching kinetics to extract gold from ammoniacal thiosulfate are improved and there are consumption of ammoniacal thiosulfate was consumed. They also study the effect of adding 0.1 and 0.8 Ml of ammonia without pulping with oxygen and found the extraction reach to 24 and 69%. While the pulping with oxygen for 1, 3, 7 1nd 22 hour increase the leaching to 81, 84, 90 and 94% respectively.

After one day of leaching with 2.37 Kg for every ton of sodium thiosulfate without oxidative ammonia pretreatment, but the pretreatment for 1 hour is negligible. The counter current of leachant contact with fresh ore give increase in the extraction of gold while the fresh leachant with pretreated ore give decrease in the extraction of gold. The leachant, other than passivation are factors that affect on the decreasing in the gold leaching rate[29].

Anderson illustrates the outlines and fundementals of leaching the alkaline sulfide solution of gold, he used special system named RECQM to identify the mechanism of leaching these results indicate that sulfide, bisulfide and polysulfide has no double effects on the system as precipitate and oxidation in the same time. Sulfide can precipitate and make complexing in the same time while polysulfide is the oxidant.

The valuable leaching must be in concentration more than 20g/l and it was found the leaching depends on the temperature where the high temperature increase the leaching and it was fount that the activation energy is 41.6 KJ/mol for both 25 g of poly sulfides and 50 g/l for sulfides.[30]



2.2. Mechanical Chemical activation of Sulfides



Figure 4: Mechanical activation system

Smekal is the first one who discovers that the ore contact with the chemical without any changes. After making mechanical activation the mineral structure is changed or the lattice is broken and divided. There are two processes occurring in the mineral or concentrate. The first one is increasing in the surface area, increase in the internal and surface energy and decrease in the coherent energy. While the second process aggregation, adsorption and recrystallization take place immediately inactivation systems that may appear during crushing or after crushing has been completed.[31]. Figure 4 indicate the mechanical activation system.

The mechanical activation with varying stages was proved previously.[32] The multistage mechanical activation need the application of crushers or mills with different application factor as the velocity of mill rotation the variety of balls the number of balls the velocity of mills. There are different factors affecting on the mechanical activation. [33&34] and different type of crushers are used also. Peter Palaz study the leaching of sulfide ore containing antimony and arsenic in the forms tetrahedrite, jamesonite, energize that dissolved in sodium sulfide then activated mechanically using two different crushing instrument the mill and attritor respectively.

After exploit copper and lead from the containing solid in pyrometallurgy, antimony and arsenic are dissolved into the leach liquor. Peter Palaz compare the conventional chemical leaching with the mechanical activation by the tetrahedrite concentrate using the industrial attritor in a process called MELT.

By comparing the mechanical activation process MELT and the direct hydrometallurgical leaching SUNSHINE, the mechanical activation several time faster. It was found that the mechanical activation in the alkaline leach solution has a positive results of the extraction of sulfides. The recovery of the metals in the mills as antimony and arsenic increased 5 times for jamesonite, about one and half time with respect to energite and four times for tetrahedrite by using the mechanical activation before dissolution in sodium sulfide solution.



The difference between chemical and mechano-chemical extraction of tetrahedrite is faster two times and half faster. The kinetic of the chemical process is slower than chemical leaching that previously mechanical activated, but it is advanced because the process in one operation step.

In the pilot plant it was compared the MELT process in which mechanically activated before leaching with the SUNSHINE process or direct chemical leaching of albeit which is more concentrated and pulp density. It is also easy to compare the crushing with mill of the freshly ore and exposing its surface with water with the other heterogeneous reaction of direct chemical.

The detail of the effect mechanical activation on the surface area and the mineral structure must be understooding the changes on the leaching kinetics, but this is complicated due to the agglomeration of the finally crushed.[35]

2.3. Pressure Leaching of sulfides

Pressure leaching is one of several leaching methods as shown in Figure 5.



Figure 5: Pressure leaching reactor

Pressure leaching is leaching method in which we use elevated temperature and pressure, to chemical dissolves valuable element or metals from the mineral or concentrate. Pressure leaching occurred in the closed reactor controlled by the temperature more than 220°C and pressure more than 20 atmospheres. The reactor that used in the pressure leaching process named autoclaves. Pressure leaching increases the dissolution of the valuable metals from ore. Pressure leaching increases the solubility of the ore due to the increase of the motion of the particles. The pressure leaching decreases the time of the reaction from 30 minutes up to 24 hours depending on the concentrate and the nature of the dissolved ore and on the conditions applied. The elevated pressure leaching considers an ideal method for the oxidative leaching. The content of the dissolved oxygen in the leach solution is directly proportional to pressure.



Usually the sulfide is converted to elemental sulfur S^0 or converted to sulfate $S_2O_4^{-2}$ in the case of converting sulfide to elemental sulfur is preferred and formed at temperatures below $120 - 150^\circ$ and required less oxidant to be added.

Two examples of pressure leaching are applied one of the pressure leaching of a mixture of cobalt and nickel sulfides the process called Sherrit Gordon process. The second pressure leaching of bauxite in the sodium hydroxide solution to produce Al_2O_3 which used in the production of aluminium by smelting electrolysis the process name is Bayer[36].

GU Yan indicate in the research how to use the pressure leaching in the laboratory range of the concentrate of zinc sulfide to produce zinc and sulfur. There are more areas need more exploration to define the relative advantages of this process and comparing with those present reasons and the advanced one.

To obtain 95% zinc and 90% sulfur it must be applied the optimum condition of the reaction that summarized as solid – liquid ratio is 1 - 4, temperature of the reaction 150° C, while the oxygen pressure 1 MPa and the grain size of the used ore is 44 mm.

Addition some additives increase the kinetics of the reaction in pressure leaching. The using of an autoclave to zinc sulfide concentrates leaching give more extraction of zinc with a decrease in the reaction time. The laboratory results give promise data for process development. [37].

2.4. Bioleaching of Sulfides

Bioleaching is dissolving of metals from their ores by using bacteria, fungi or algea. Bioleaching considers a new clean process compared with the other known methods as heap leaching using cyanide. Bioleaching is one of promising of several methods of biohydrometallurgy and different processes is used to obtain some metals as copper, zinc, lead, arsenic, antimony, nickel, molybdenum, gold, silver, and cobalt.

Bioleaching can include numerous types of oxidizing bacteria, including acidobacillus ferrooxidans which known previously as bacillus ferrooxidans and acidobacillus thiooxidans which also known as bacillus ferrooxidans. Generally ferric ion used to oxidizing ore. This step is independent of the action. The role of bacteria is further oxidizing the ore and also regenerate the chemical of oxidant as Fe^{2+} and Fe^{3+} for example, bacteria catalyst to break down pyrite (Fe₂S) by oxidizing sulfur and metal. (in case of ferrous iron, Fe^{2+}) using oxygen. This produces soluble products rhat can be further purified and reproduce the demand product. The bioleaching illustrated in Figure 6.



Figure 6:Bioleaching system



Comparing the bioleacing process with the traditional one. The traditional leaching needs extra steps as roasting, oxidation, pressure, smelting and required concentrated ore all those steps are expensive and environmentally unfriendly.

Advantages

- 1- Low grade ore doesn't represent any problems with bioleaching extraction because it ignores the impurities surrounded the metal needed. In some elementes about 90% are recovered.
- 2- Microorganisms gain energy from the breaking down of the element that formed minerals. The company simply collects the ions after bioleaching,
- 3- The process is very simple as comparing with the traditional one.
- 4- Bioleaching is specific for certain types of ore, bioleacing not complicated leaching process and need less experts for the operating system.
- 5- Bioleaching is more envrironment friendly compaired with the traditional ones.

With respect to company, this can be translated to profit because the decreasing of SO_2 gas evolving during the smelting is expensive. Also, some landscape damage occurs. Also, bacteria grow naturally and the mine and surrounding area left relatively untouched. When bacteria bread in the condition of the mine, it can be cultivated and recycled easily.

Ore concentrates: Bioleaching treat the low grade ore or the waste and not need grinding or crushing all those need huge costs and energy consuming.

Disadvantage

- 1- Economics: The bioleaching is very slow comparing with known processes as smelting or direct leaching, it lead also to loss and decrease in the currency
- 2- Also some toxic chemicals can penetrate to the earth, which harm the under ground water and convert it to acidic, which cause harmful to the environment. When there is an increase in the pH due to the dilution with fresh water some ions are precipitate which leads to pollution of "Yellow Boy"
- 3- For the previous reasons it must be planned for the biological process. The bioleaching without planning may be led to biosafely failure.
- 4-We can not stop the heap leaching because it continues with the rain water and natural bacteria.[38].

Natalya et al use the biogenic ferric iron to study the leaching of copper zinc from different sulfide ores concentrates. He also used sulfide ore concentrates as chalcopyrite, spharilite, pyrohotite and pyrite with the concentration range of 29-55, 3.9 - 11, 14 - 34 Ind 12 - 13 respectively.

The rate of copper leaching was shown decrease from 5.1 - 2.6g/l/h and the concentrate from 10.1 - 19.2 and the leaching of zinc from 2.9 - 5.3g but an increase in concentration from 2.64 - 7.36. Some results that copper leaching without change in range, from 0.2 - 0.27 g/g/h. We suppose that this was collected on the dependent of factors on the rest potential of chalcopyrite. The dissolution of zinc ranged from 0.73 to 1,14 g/g/h and depend significally on sulfide contents in the mineral.

The leaching rate increase with increase the chalcopyrite in concentrate. At the same time there is a galvanic reaction occurs between metals. Chalcopyrite and pyrite have high potential while spharilite and pyrohotite have low potential. It was improved the prediction possibility of efficiency of removal of zinc and iron through the leaching of copper zinc concentrate was depend mainly on the sulfide mineral content [39].

Tariq et al said now a day it is economically to smelt copper ore instead of leaching because ore dressing of copper is costly in general. The income of smelting indicate the cost. In the largest mine all over the world "Escondida in Chile ore dressing of gold in its ore is very low. Bioleaching cost is overcome the mining time of extraction of metals. The ore dressing of ore is very costly, number of companies try to keep up with demand and end up with dept. Some projects proved as finish Talvivaara that the process economically disastrous either is or environmentally in this study the data collected through black chist with a different leaching process to measure the effect of pH and ORP on chemical and bacterial leaching.

Without pH control or from pH 3.0 - 3.8 and without bacteria the ability of dissolution Ferric ion is very limited. All Fe dissolves in Ferrous due to decrease in ferric ion by the ore. At the pH 1.5 control dissolution of iron increased, but dissolved iron presen as ferrous due to the absence of oxidizing bacteria.

The relatively high value of ORP due to the corresponding inoculate trues, due to the dominance of Fe^{3+} on Fe^{2+} . Higher recovery of metal from black chist produced due to biotec systems more than abiotic due to the pH control. Nickel and zinc solubilize in a wide range of pH compared with copper and cobalt. Copper ion recovery remains less than the other metals.



The obtained data indicate that chalcopyrite passivation by the formation of jarosite and elemental sulfur as a by product solid phase. The Secondary stage of gypsum coated by tin with the highest metal recovery, and vermiculite, which is developed product in the last stage of biotite/phologopite mica stage.

X-ray diffraction pattern indicates that the beak of sulphide is weak below the etection [40]

Chen et al found that 1. Aeration effect on the bioleaching rates of Ni and Mo theleaching experiment of MBR indicate that the optimum aeration condition is 1 l/min., 2.The concentration of Mo is 395mg/l is the optimum to reach the maximum leaching of Ni and Mo, the concentration mentioned in MBR avoid the toxisity of microbe, also iron play a role in oxidation of metal., and 3. Leaching of Ni is greater than Mo due to the mineral structure, crystal lattice, ion surface energy, potential, conduction and so on [41].

Yu-ting et al 2018 found that leaching rate of chalcopyrite by using S. metallicus bacteria is a little higher than A.Brierleyi and also both strains is higher in leaching of chalcopyrite than each one singly. The community structure analysis during the leaching indicate that the S. metallicus are stable in the structure analysis, also A. brierleyi indicate increase trend changes in the concentration of copper in the leachant were due to the fast increase in leaching of mixed archaea compared with single archea. Analysis of Langmuir competitive adsorption between two thermophilic archea. Moreover PCR confirmed that adsorption promotion occurred between S. metallicus bacteria and A. brierleyi in mixed system [42].

III. SILICATES

3.1. Leaching of silicate

Eliana et al proved experimentally on leaching of metakaoline by hydrofluoric acid to dissolve Aluminium and silicate. And recovery reaches to 96% at the following optimum conditions 330 RPM, 12% v/v, solid/lqiuid ratio 2%, reaction time 2 hour and temperature of reaction is 348 K.

After alkali chemical precipitation, the recovery of aluminium and silicon is achieved 99% of silicon and 70% of aluminium, also ctyolite with 89.3% purity.[43].

3.2. Bioleaching of Silicate

The bioleaching mechanism by using B. mucilaginosus depends mainly on K^+ release or any other element from the silicate mineral.

Yakhontova suggested that decomposition of silicate mineral by bacteria depends mainly on the structure and chemical composition [44].

Grudev make experiment to indicate the release of K^+ from silicate mineral and suggest the presence of mucilaginous capsule consists of exosuccharides by bacteria leads to mineral dissolution[45]. Vainberg suggested also the dissolution of metal due to the production of organic acids in culture media [46]. Also, there is a paucity in experimental data support hese hypothesis. The present study indicates the leaching of K^+ and SiO₂ from silicate minerals by using B. mucilaginosus bacteria as a result the exosuccharide and organic acid are produced.

Some organic acids as oxalate and citrate produced by mucilagnosus that form biodentate complex with metal ions which is more reactive compared with monodentate complex which is formed by acetate and propionate [47].

Bacteria reproduction produce polysacchrides and this can be combined with mineral to form bacteria-mineral complexes. An area of high concentration of organic acid is formed near the minerals due to the strong absorption of polysaccharides to the organic acids. The mineral degraded due to the effect of organic acids, on the other hand polysaccharide absorb SiO₂ and O₂. The variation of concentration of SiO₂ affect on the balance between two stages of metals the stage of reaction between SiO₂ and K+ which leads to mineral degradation.[48].

The manufacture of glass, quartz sand in Slovak is the most important raw materials and also the amount of iron oxide which is allowed is varied from 0.012 - 0.02. The metals carry iron can be removed by magnetic separation also it is difficult to separate the very fine iron particles by traditional methods of removal. The bioleaching is attraction method for removal of metals. The bioleaching for four months using molasses make the process uneconomic. Bioleaching need short courses and remove about 60% at least of iron from sand quartz.

The optimization of AQDS and iron complexing agent may be adjusted to be useful. In previous study with Aluminium silicate and isolated bacillus species, oxalic, acetic, lactic, pyruvic, butyric and formic acid were found in the consumption media[49&50]. Several experiments are done to confirm that Bacillus species is suitable for bioleaching of quartz sand by dissolving calys and iron minerals from quartz surface. To supply the biomass still iron removal a main kinetic problem, it must be developed for balancing treatment quartz sand [51].



Mark et al proved the importance of mineralogy in silicate mineral specially that contained in low grade sulfide ores that may consider in heap bioleaching they also proved that the dissolution of raw elements as fluorine from silicate mineral phase prevent the reproduction of bacteria present during the bioleaching, the problem of acid consumption and precipitation of silica "Jelly like" cost effective. To overcome those problems it must be used the heap leaching and pH control of liquor[52].

Jiangman study: 1 - the effect of ba cteria known as Paenibacillus mucilaginosus BM-4, he adapted in this paper the acidity and the temperature with the mineral of layer crystal structure as kaolinite and chlorite., 2- Study the adsorption of BM-4 on bauxite and kaolinite he found that kaolinite is adsorbed electrostaticlly by bacteria BM-4 while bauxite adsorbed as langmiur isotherm., 3 - The flotation recovery of kaolinite increase from 50% to 65.3 -77.3 while it decreases with Bauxite from 48.9 to 25.7 -27.8, also the kaolinite surface become hydrophobic while the bauxite surface become hydrophilic due to the interaction with bacteria BM-4., 4 - The flotation experiment was done on the mixture of bauxite: kaolinite with ratio 5:1 by using bacteria BM-4 using modified Hallmond tube, the results indicate increase the ratio of Al/Si from 3.05 - 8.06 and alumina recovery reach to 83.0%.[53]

Xiaoxi et al found that Bioleaching of silica using glucose and ammonium sulfate as carbon and nitrogen source, respectively, as optimum energy sources, the cell count or an inoculums percentage from 1% to 5% has a little different effect on desilication. The dissolution of silica by the bacteria increase by decreasing of grain size, the optimum temperature and RPM are 30°C and 220. The optimum conditions were appropriate to the strains, growth, which help the strains to bioleaching[54].

IV. CONCLUSION

The aim of his review is giving spots on the new processing of minerals in the few last decades, and also define the new directions for leaching of sulfides and silicates minerals also given an idea about the occurance of the ores in Egypt. It was also given a spot about the new technologies of sulfides minerals processing (leaching, mechanical activation, pressure leaching, and bioleaching) and silicate mineral processing (leaching and bioleaching). The main concern in this review on reaction of sulfides and the behavior of iron and pyrite in leaching of sulfide ores. (1) The two common Fe-sulfides, pyrite and pyrrhotite, display distinctly dissimilar reaction pathways in the oxidative leaching process. The leaching of pyrite, sulfur oxidized to elemental sulfur under comparable conditions. The main direction of leaching pyrohotite unoxidized sulfide oxidized to sulfur and can also oxidized to sulfate.

Due to the low solubility of Cu-sulfide, the nonoxidative sulfide disintegration may have an adverse effect on Cu leaching. Pyrite oxidation is strongly acid producing, while pyrohotite oxidation produces acid only via the subsequent hydrolysis of dissolved ferric iron, thereby impacting the acid balance of a leaching process.

The new results indicated that the ferric iron-mediated indirect mechanism is an important part of the bacterial leaching process of sulfide minerals.

(2) Galvanic coupling of pyrite and chalcopyrite enhanced chalcopyrite leaching. This effect may be masked by the kinetically favored pyrite oxidation at high solution redox potentials.

Silver was an effective catalyst in the bacterial leaching of chalcopyrite. A catalytic effect on Cu dissolution was also observed by adding graphite into the leaching system, or by suppressing the solution redox potential. These observations underscore the importance of the electrochemical processes in the bacterial leaching of sulfide minerals.

(3) The bacterial leaching rates displayed dissimilar temperature dependence, suggesting that the ratedetermining steps were mineral-specific. The high apparent activation energy value of pyrite oxidation indicated that a chemical reaction was the rate determining step, while lowering the activation energy of pyrohotite indicated diffusion control.

Two modified kinetic models, a shrinking core model and shrinking particle model, were used to derive the rate equations for pyrrhotite and pyrite oxidation, respectively. Research on mineral-specific physical and chemical processes which control the oxidation of sulfide minerals serves an essential basis for the modelling and computer simulation to develop, scale-up systems and to elucidate the biogeochemical reactions of sulfide minerals in natural ambient environments.

REFERENCES

- F. Habshi "Recent trends in extractive metallurgy" Journal of Mining and Metallurgy 45 B(1) 2009 1-13.
- [2] Guilbert, John M. and Charles F. Park, Jr. (1986) The Geology of Ore Deposits, W. H. Freeman, p. 1.



- [3] Guilbert, John M. and Charles F. Park, Jr. (1986) The Geology of Ore Deposits, W. H. Freeman, p. 1.
- [4] El-Shazly , E.M. Farag. I.A. M. and Bassyouni, F.A. 1965, Contribution to the Geology and minerlization of Abu Sawayel area, Eastern Desert. Part I- Geology of Abu Swayel area: Egyptian Journal of Geology, 9, 45 – 67.
- [5] "Mineral Silicates". britannica.com. Archived from the original on 25 October 2017. Retrieved 8 May 2018.
- [6] Deer, W.A.; Howie, R.A.; Zussman, J. (1992). An introduction to the rock-forming minerals (2nd ed.). London: Longman. ISBN 0-582-30094-0.
- [7] Hurlbut, Cornelius S.; Klein, Cornelis (1985). Manual of Mineralogy (20th ed.). Wiley. ISBN 0-47180580-7.
- [8] A. F. Amer et al "Assessment of the Egyptian Clay Deposit" Studies on Some Mineral Deposits of Egypt" Edited by Mohgoub, O.M. p260, 1970.
- [9] N. N. Yamni "Characteristics of lower cretaceous kaolin deposits, West Central Sinai" Egypt, I. Geolgy, V.31, 1-2, ppI29-141, 1987.
- [10] A. Youssef "Final Report" Up-grading of Egyptian Kaolin to meet specifications for Paper and ceramic industries "STC, Academy of scientific and technology, Cairo, Egypt, July, 1994.
- [11] A.A.Abdel-Maksoud, «Mineralogical and geochemical specifications of raw materials and their role in the blue brick industry, MSc thesis, faculty of science, cairo univ., 1992.
- [12] A. Dartlccr, "Raw materials for ceramics industry in Egypt", 1992
- [13] A.Was "feldspars substitutes in Arab Republic of Egypt",12th Annu. Meat. Mineralog. Soc. Egypt, p. I 5 Dec. 1998.
- [14] A.M.Hussien, "Beneficiation of some Egyptian Nepheline syanite ores for ceramics and glass industries" M.Sc. Thesis, Faculty of Eng., Cairo Univ 1998.
- [15] M.F. El-Ramly, c c The three ring Complexes of Gabal EI Kahfa, Gabal Nigruib EI Fogani and Gabal EI Naga" A Geological Survey of Egypt, 1969.
- [16] Suprem Counc. Univ. "Evaluation and classification of Egyptian sand and clay minerals for industrial uses "Evalu. Classif.Egypt sand clay Min.Indust. Uses. Cairo, Egypt, FRCU 211d report, no.2, p.157, 1988.
- [17] A.K Hassan, "Glass sand in Egypt proceed .symp Product Develop. Mineral Products", Ceramics, Refractories, Ferroalloys, Cairo, Egypt.pp.10-25, Dec.1993.
- [18] A. A. Dardeer, "Raw materials for ccranuc industry in Egypt", Gcol.Surv.Egypt., 15 scpt., 1990.
- [19] "Beneficiation of silica sand, flows heel study", Denver Bull., 1968 .
- [20] Geol. Surv., "Unitilization of Egyptian talc-magnesite and dolomite raw materials for the production of some types of basic refractories" Progress report II, To Acad. Sci. Res. Tech 1992.
- [21] A. Bishai, et al, "Blacksand deposits", geological Surv., Egypt, No. 61. Pp 63 – 66, 1974.
- [22] Um, Namil (July 2017). Hydrometallurgical recovery process of rare earth elements from waste: main application of acid leaching with devised diagram. INTECH. pp. 41–60.
- [23] Briones, R., Lapidus, G.T., 1998. Leaching of silver sulfide with the thiosulfate- ammonia-cupric ion system. Hydrometallurgy 50 (3), 243–260.

- [24] Trejo-Gallardo, J., Lapidus, G.T., 2005. Mathematical model for the leaching of acanthite in thiosulfate solutions. In: Dixon, D.G., Dry, M.J. (Eds.), Proceedings of the 1st Symposium on Computational Analysis in Hydrometallurgy (44th Annual COM). Met Soc CIM, Calgary Alberta, pp. 429–441.
- [25] Jared L. Deutsch and David B. Dreisinger, "Silver sulfide leaching with thiosulfate in the presence of additives Part I: Copperammonia leaching", Hydrometallurgy, 137 (2013 156 – 164.
- [26] Jared L. Deutsch and David B. Dreisinger, "Silver sulfide leaching with thiosulfate in the presence of additives Part II: Ferric complexes and the application to silver sulfide", Hydrometallurgy, 137 (2013) 165 – 172.
- [27] Tao Chen Chang Lei, Bo Yan, Xianming Xiao aJared L. Deutsch and David B. Dreisinger, " Metal recovery from the copper sulfide tailing with leaching and fractional precipitation technology ", Hydrometallurgy, 147 - 148 (2014) 178–182.
- [28] Mari Lundström, Jussi Liipo, Pekka Taskinen, Jari Aromaa " Copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions", Hydrometallurgy, 166 (2016) 136 – 142.
- [29] D. Feng J.S.J. van Deventer "Oxidative pre-treatment in thiosulphate leaching of sulphide gold ores", International Journal of Mineral Processing 94 (2010) 28–34.
- [30] C.G. Anderson "Alkaline sulfide gold leaching kinetics", Minerals Engineering 92 (2016) 248–256.
- [31] A.G. SmekalZum mechanischen und chemischen Verhalten von Calcitspaltflächen Naturwissenschaften, 39 (1952), pp. 428-429
- [32] A.Z. Juhasz Mechanochemical activation of silicate minerals by dry fine grinding Aufbereitungs-Technik, 10 (1974), pp. 558-562
- [33] V.I. Molčanov, O.G. Selezneva, E.N. ŽirnovActivation of Minerals by Grinding Nedra, Moscow (1988).
- [34] P. Baláž Mechanical activation in technology of metals extraction Metall, 54 (2000), pp. 190-195.
- [35] Peter Baláž and Marcela Achimovičová "Mechano-chemical leaching in hydrometallurgy of omplex sulphides", Hydrometallurgy 84 (2006) 60 – 68.
- [36] GU Yan, ZHANG Tingan, LIU Yan, MU Wang-zhong, ZHANG Wei-guang, DOU Zhihe, JIANG Xiao-li), "Pressure acid leaching of zinc sulfide concentrate", Trans Nonferrous Met. Soc.China 20(2010)s136-s142.
- [37] Brandl H. (2001) Microbial leaching of metals. In: Rehm H.J. (ed.) Biotechnology, Vol. 10. Wiley-VCH, Weinheim, pp. 191–224
- [38] Watling, H.R. (2006). "The bioleaching of sulphide minerals with emphasis on copper sulphides — A review". Hydrometallurgy. 84 (1–2): 81.
- [39] Natalya V. Fomchenko, Maxim I. Muravyov " Effect of sulfide mineral content in copper-zinc concentrates on the rate of leaching of non-ferrous metals by biogenic ferric iron", Hydrometallurgy, 185 (2019) 82 – 87.
- [40] Tariq M. Bhatti, Jerry M. Bigham, Antti Vuorinen, Olli H. Tuovinen, "Chemical and bacterial leaching of metals from black schist sulfide minerals in shake flasks", International Journal of Mineral Processing 110 – 111(2012) 25–29.



- [41] CHEN Jia-wu, GAO Cong-jie, ZHANG Qi-xiu, XIAO Lian-sheng, ZHANG Gui-qing, "Leaching of nickel-molybdenum sulfide ore in membrane biological reactor", Trans Nonferrous Met. Soc.China 21(2011) 1395 – 1402.
- [42] Yu-ting LIANG, Jun-wei HAN, Chen-bing AI, Wen-qing QIN "Adsorption and leaching behaviors of chalcopyrite by two extreme thermophilic archaea", Trans Nonferrous Met. Soc.China 28(2018) 2538 – 2544.
- [43] Eliana G. Pinna, Daniela S. Suarez and Gustavo D. Rosales "Hydrometallurgical extraction of Al and Si from kaolinitic clay" REM, Int. Eng. J., Ouro Preto, 70(4), 451-457, oct. dec. | 2017.
- [44] Yakhontova LK, Andreev PI, Ivanova MY, Nesterovich LG. 1987 Bacterial decomposition of smectite minerals. Doklady Akademii Nauk SSSR 296, 203–206
- [45] Grudev S. 1987 Use of heterotrophic microorganisms in mineral biotechnology. Acta Biotechnol 7, 299–306.
- [46] Vainberg SN, Vlasov AS, Skripnik VP. 1980 Enrichment of clay raw material using silicate bacteria. USSR Tr.-Mosk. Khim. Tekhnol. Inst. im. D.I. Mendeleeva 116, 34–37.
- [47] Welch SA, Ullman WJ. 1993 The effect of organic acids on plagioclase dissolution rates and stoichiometry. Geochimica et Cosmochimica Acta 57, 2725–2736.
- [48] Wuxing Liu, Xushi Xu, Xianghua Wu, Qiyin Yang, Yongming Luo & Peter Christie "Decomposition of silicate minerals by Bacillus mucilaginosus in liquid culture", Environmental Geochemistry and Health (2006) 28:133–140.

- [49] Štyriaková, I., Štyriak, I., Kušnierová, M., 1999. The release of sulphidic minerals from aluminosilicates by Bacillus strains. In: Amils, R., Ballester, A. (Eds.), Biohydrometallurgy and the Environment toward the Mining of the 21st Century. Elsevier, Amsterdam, pp. 587–596
- [50] Štyriaková, I., Štyriak, I., Malachovský, P., Lovás, M., 2006. Biological, chemical and electromagnetic treatment of three types of feldspar raw materials. Miner. Eng. 19, 348–354
- [51] Iveta Štyriaková, Igor Štyriak, Pavol Malachovský, Zbyněk Večer, Dávid Koloušek, "Bacterial clay release and iron dissolution during the quality improvement of quartz sands", Hydrometallurgy 89 (2007) 99 – 106.
- [52] Mark Dopson, Anna-Kaisa Halinen, Nelli Rahunen, Dan Bostro" m, Jan-Eric Sundkvist, Marja Riekkola-Vanhanen, Anna H. Kaksonen, Jaakko A. Puhakka "Silicate Mineral Dissolution During Heap Bioleaching" Biotechnology and Bioengineering, Vol. 99, No. 4, March 1, 2008.
- [53] Jiangman Zhao, Weijin Wu, Xu Zhang, Minglong Zhu, Wensong Tan, "Characteristics of bio-desilication and bio-flotation of Paenibacillus mucilaginosus BM-4 on aluminosilicate minerals" International Journal of Mineral Processing 168 (2017) 40–47.
- [54] Xiaoxi Zeng1,2,a, Hongbo Zhou 2 ,Yuehua Hu 2, Jianxin Tang1,b, Pei Jiang1, Wen Li1, "Study on the influence factors of desilication in bioleaching by B. mucilaginosus", Advanced Materials Research. Vols. 415-417, (2011) pp 1740-1743.