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New Trends of Leaching of Silicate and sulfide Minerals

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Abstract **– Although ore processing is an old technique, it is still the technique used to treat sulfide or silicate ores, a traditional and prevalent technique. Silicate ores treated thermally include kaolin, clay, feldspare, nepheline syenite, silica sand, quartz, talc and zircon. Sulfide ores include chalcopyrite, pyrite. The technique is facing challenges through new mineral hydrometallurgical processes. The new trends as hydrometallurgy, mechanical activation, pressure leaching and bioleaching are discussed in the present review article and compared with each other for both sulfides and silicate ores.**

I. INTRODUCTION

The role of science and technology in economic development is continuously increasing. New trends in material science including mineral processing focus on economization of the existing technologies as well as 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 and environmentally friendly and do not require sophisticated machinery. The present article deals with 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 recover valuable metals from ores as sulfides and silicates different technique are required. Physical, physico-chemical and mechanical techniques are used in mineral processing. Chemical processing or extractive metallurgy is divided to hydro- and pyrometallurgy.

Electro-metallurgy is the most recent technology and came into existence only after exploring of large-scale electrical generator in the of mid nineteenth century. Hydrometallurgy is recently applied four hundred years, while pyrometallurgy is the oldest technology. [1]

II. ORES AND OCCURRENCES

An ore is a natural rock or sediment that contains sufficient minerals with economically important elements, typically metals, that can be economically extracted from the deposit[2]. The ores are extracted at a profit from the earth through mining; they are then refined future processing to extract the valuable element, or elements.

The ore grade, or its concentrates as well as its mode of occurrence, will directly affect the costs associated with mining. The cost of extraction must thus be weighed against the metal value contained in the rock to determine what ore can be processed and what ore is of a too low grade to be worth mining. Metal ores are generally oxides, sulfides, silicates, or native metals that are not commonly concentrated in the Earth's crust, or noble metals (not usually forming compounds) such as gold. The ores must be processed to extract the elements of interest from the waste rock and from the ore minerals. Ore bodies are formed by a variety of geological processes. The process of ore formation is called ore genesis.

2.1. Sulfide ores in Egypt

The class of minerals containing S^{-2} as a major anoin are named sulfide minerals. Some of these minerals are important because they contain a precious metals as gold or silver.

The sulfide minerals are a class of minerals containing sulfide or persulfide as the major anion. Some sulfide minerals are economically important as metal ores. The sulfide class also include the solenides, the tellurides, the aresenites, the antimonsdes, the bismusthunides and sulfo salts.

Sulfide minerals are the main source of the elements, lead, zinc and copper.

In Egypt the minerals are divided into four main types:

The first type is named seposite which contains lead and zinc sulfides.

The second type contains copper or nickel with cobalt which is present in Abu Swayel in South Eastern Desert.

The third type contains copper – nickel sulfide deposits. This type of mineralization occurs in Layered mafic-ultramafic instructions like gabbro in Akarem and El Geniene and the fourth type is zinc, copper lead deposits 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.

Figure 1: Photos of some sulfide ores

2.2. Silicate Ores in Egypt

Silicate minerals are rock-forming minerals made up of silicate groups. They are the largest and most important class of minerals and make up approximately 90 percent of the Earth's crust.[5-7]

Figure 2: Photos of some silicate minerals

A- Kaolin ($Al_2Si_2O_5(OH)_4$

Kaolin is found in Egypt in three main localities, Sinai, along the Red Sea Coast and Wadi Kalabsha near Aswan. The estimated reserves in Sinai is about 100 million tons, [8-10] most of Sinai Kaolin is used in ceramic and sanitary industries.

B- Clays (Hydrous Aluminum Phyllosilicate)

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

C- Feldspare ($KAlSi_3O_8$, $NaAlSi_3O_3$)

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

D- Nepheline Syenite(Anhydrous Sodium Potassium Alumino Silicate)

Nepheline Syenite is present in southern sector of the Eastern Desert, south Idfu Marsa Alam Road[14&15].

E- Sandstone

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

F- Talc ($Mg_3Si_4O_{10}(OH)_2$

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

G- Zircon ($ZrSiO_4$)

Zircon reserves are present along the medetranian sea specially in the region between Rosetta and Damiatta on the sea coast[21].

III. CHEMICAL PROCESSING OF SULFIDES

3.1. Leaching of Sulfides

Leaching is the process of extracting substances from a solid mixture by dissolving them in a liquid.

Figure 3: Leaching reactor

In a primary dissolving process in hydrometallurgical operation, the metal transfer from the mineral to aqueous solutions. In fact, there is selective dissolution of the valuable metal from the ore, concentrate or matte by the reaction with the active chemical solution. Because the dissolution is selective so most of the impurities are not dissolved [22].

After the leaching process the metal is separated from the solution by filtration. The solution is named pregnant solution or leach liquor. The solid product is known as residue or tailings.

Silver sulfide leaching

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

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

Cupric-tetraamine complex is stable in solution giving 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.

The very low concentration of copper is suggested under the chemical diffusion control. The chemical control may be a result of driving force. The study of low concentration of copper needs more efforts [23&24].

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

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

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

Kinetically these three complexes were slow. The Ferric – EDTA show the best complex for the commercial implementation. Ferric – citrate is the slowest one for silver sulfide leaching and is used at low pH.

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

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

The low leaching results of silver by thiosulfate is related to the mineralogical form under the conditions tested. This illustrates 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 or anaerobic environment in presense or absence of EDTA.

In aerobic environment, the acceleration of leaching decreases 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.

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

Copper Sulfide

The metal recovery from copper sulfide tailing depends 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 extracted 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 treated the sludge using sulfuric acid at the ambient pressure. 0.24 ml/g of H_2SO_4, S:L of 1:2, stirring velocity 400 RPM, and the extraction time reachs 2 hours. The leaching of the elements from the sludge Cu, Zn, Mn, and Fe reach 19.53%, 33.48%, 14.10% and 49.13% respectively.[27]

After treatment of the tailing of copper, 95.45%, 93.74%, 89.70 and 93.29 for the metals Fe, Cu, Zn and Mn respectively have been leached. These elements coud be extracted from the sludge with 49.13%, 19.53%, 33.48% and 14.10 [27].

Mari et al study the leaching of four different chalcopyrite samples from different mines around the world, copper sulfide is dissolved in concentrated copper chloride. They found that for the four samples iron and copper precipitate with different ratios not with equal ratios as expected. She also found that oxygen leads to precipitation of covelite.

Extraction of bornite has no effect on the acidity and no strong copper precipitation was observed.[28]

Gold Sulfide

Pretreatment by oxidative ammoniacal solution was studied by Feng and Van Deventer. The overall leaching kinetics to extract gold from ammoniacal thiosulfate were improved with consumption of ammoniacal thiosulfate. They also studied the effect of adding 0.1 and 0.8 ml of ammonia without pulping with oxygen and found that the extraction reachs to 24 and 69%. Upon Pulping with oxygen for 1, 3, 7 1nd 22 hours increased the leaching to 81, 84, 90 and 94% respectively.

After one day of leaching with 2.37 Kg sodium thiosulfate for every ton ore without oxidative ammonia pretreatment, but the counter current contact of leachant with fresh ore gave increase in the extraction of gold while the fresh leachant with pretreated ore gave decrease in the extraction of gold. This 2-step counter-current leaching process proved that the leachant, other than the passivation, was the determinant factor causing the gold leaching rates to decrease after a certain time of leaching. The findings enable the thiosulphate leaching of high sulphide containing gold ores to be more efficient at lower thiosulphate consumption following the oxidative ammoniacal pre-treatment [29].

Anderson illustrates the outlines and fundamentals of leaching the alkaline sulfide solution of gold, he used special system named rotating electrochemical quartz crystal microbalance (RECQM) to identify the mechanism of leaching. The results indicate that; sulfide, bisulfide and polysulfide has no double effects on the system as precipitate and oxidation take place in the same time. Sulfide can precipitate and make complex ion in the same time while polysulfide is the oxidant.

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

3.2. Mechanical Activation of Sulfides

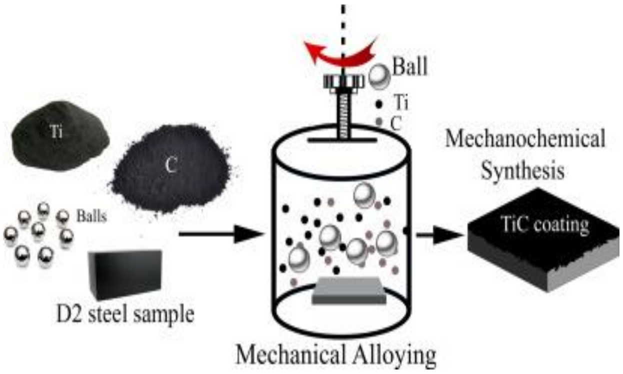

Figure 4: Mechanical activation system

Smekal is the first one who discovered that just contacting the ore with the chemical no change was observed. After 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 the surface area and increasing the internal and surface energy and decreasing the coherent energy. While the second processes aggregation, adsorption and recrystallization take place immediately indicating inactivation that systems that may appear during crushing or after crushing has been completed[31]. Figure 4 indicates 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.

Peter Palaz studied the leaching of sulfide ore containing antimony and arsenic in the forms tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$, jamesonite ($Pb_4FeSb_6S_{14}$), energite (Cu_3AsS_4) dissolved in sodium sulfide then activated mechanically using two different crushing instrument the mill and attritor respectively.

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. SUNSHINE process with relatively small differences in leach conditions can bring important economical benefits for the whole technology. The mechanical activation for several times is faster. It was found that the mechanical activation in the alkaline leach solution has a positive result in 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 energy 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.

It is possible that freshly exposed mineral surfaces undergo surface reactions with water or the grinding media in the grinding mill which differ from the direct heterogeneous reactions that occur with combined mechano-chemical leaching.

More detailed studies are required to compare particle size distributions before and after mechanical activation to try to understand and quantify changes in leach kinetics in terms of surface area as well as mineral structure, but this is complicated by the agglomeration of finely ground particles.

In the pilot plant it was compared between the MELT process in which the ore was mechanically activated before leaching with the SUNSHINE process or direct chemical leaching. 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 treatment.

The details of the effect of mechanical activation on the surface area and the mineral structure must be understood in view of the changes on the leaching kinetics, but this is complicated due to the agglomeration of the finely crushed ore[35].

3.3. Pressure Leaching of sulfides

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

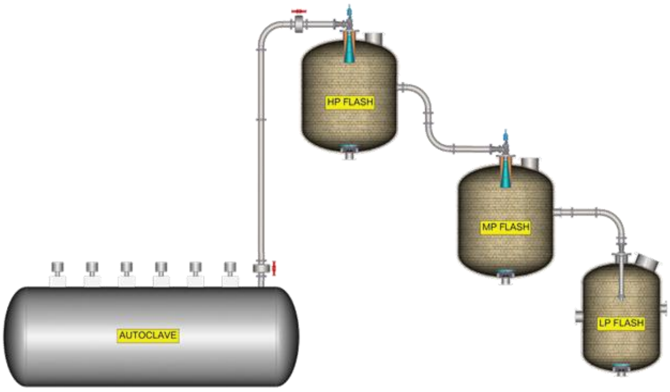

Figure 5: Pressure leaching reactor

Pressure leaching is a leaching method under elevated temperature and pressure, to chemically dissolve valuable element or metals from the mineral or concentrate. Pressure leaching occurres in the closed reactor controlled by a temperature more than 220°C and pressure more than 20 atmospheres. The reactor used in the pressure leaching process are named autoclaves. Pressure leaching increases the dissolution of the valuable metals from the 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 depending on the concentrate and the nature of the dissolved ore and on the conditions applied. The elevated pressure leaching is considered 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 SO_4^{-2}. Converting sulfide to elemental sulfur is preferred and is formed at temperatures below 120 – 150° and requires less oxidant to be added.

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

GU Yan indicated in a 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 other processes.

To obtain 95% zinc and 90% sulfur under the optimum condition of 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 µm.

The addition of some additives increases the kinetics of the reaction in pressure leaching. The uses of autoclaves for zinc sulfide concentrates leaching gave more extraction of zinc with a decrease in the reaction time.The laboratory results gave promise data for process development.[37].

3.4. Bioleaching of Sulfides

Bioleaching is dissolving of metals from their ores using bacteria, fungi or algea. Bioleaching is considered a new clean process compared with the other known methods as heap leaching using cyanide. Bioleaching is one of the promising methods of biohydrometallurgy and different processes are 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 known previously as bacillus ferrooxidans and acidobacillus thiooxidans which also known as bacillus ferrooxidans. Generally ferric ion is used to oxidize the 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 (Fe_2S) by oxidizing sulfur and metal. (in case of ferrous iron, Fe^{2+}) using oxygen. This produces soluble products that can be further purified and reproduce the demand product. The bioleaching process is illustrated in Figure 6.

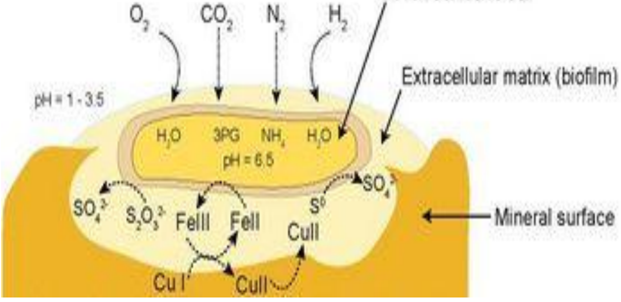

Figure 6: Bioleaching System

At. ferrooxidans binds to a metal sulfide substrate by way of an extracellular polymer matrix. The redox cycling conducted in the matrix helps to sustain the bacterium. [38]

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 surrounding the metal needed. In some elements the element recovery is 90%.
2. Microorganisms gain energy from the breaking down of the element forming minerals.
3. The process is very simple as compared with the traditional one.
4. Bioleaching is specific for certain types of ore, bioleacing is not complicated leaching process and needs less experts for the operating system.
5. Bioleaching is more envrironment friendly compaired with the traditional ones.

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.

Bioleaching treat the low grade ore or the waste and do not need grinding or crushing which need huge costs and energy consuming.

Disadvantage

6. Economicelly The bioleaching is very slow comparing with known processes as smelting or direct leaching.
7. Also some toxic chemicals can penetrate to the earth, which harm the under ground water and convert it to acidic, which is harmful to the environment. When there is an increase in the pH due to the dilution with fresh water some ions are precipitated which leads to pollution.
8. Do not stop the heap leaching because it continues with the rain water and natural bacteria.[39].

Natalya et al used 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 1nd 12 – 13 respectively.

The rate of copper leaching decreases 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 show that copper leaching is without change in the range from 0.2 – 0.27 g/g/h. The dissolution of zinc ranges from 0.73 to 1,14 g/g/h and depends significally on sulfide contents in the mineral.

The leaching rate increases with increase of 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. The efficiency of removal of zinc and iron through the leaching of copper, zinc concentrate depend mainly on the sulfide mineral content [40].

Tariq et al claimed that it is economic to smelt copper ore instead of leaching because ore dressing of copper is costly in general. In the large mine all over the world Escondida of in Chile ore dressing of gold in its ore is very low. Bioleaching cost overcomes 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 is disastrous either economically or environmentally.

Without pH control or from pH 3.0 – 3.8 and without form bacteria the ability of dissolution of ferric ion is very limited. All Fe dissolves in ferrous due to decrease in ferric ion by the ore. At pH 1.5 control dissolution of iron increased, but dissolved iron present as ferrous due to the absence of oxidizing bacteria[41].

Chen et al found that

1. Aeration effect on bioleaching rates of Ni and Mo the leaching experiment of MBR (Membrane Bioreactor) indicate that the optimum aeration condition is 1 l/min.,

2.The concentration of Mo is 395 mg/l is the optimum to reach the maximum leaching of Ni and Mo, the concentration mentioned in MBR avoid the toxcisty of microbe, also iron plays a role in oxidation of metal.

3. Leaching of Ni is greater than Mo due to the mineral structure, crystal lattice, ion surface energy, potential, conduction and so on[42].

Yu-ting et al found that the leaching rate of chalcopyrite using S. metallicus bacteria is a little higher than A. Brierleyi and also both strains are higher in leaching of chalcopyrite than each one.

The community structure analysis during leaching indicate that the S. metallicus are stable in the structure analysis, also A. brierleyi indicate increased trend changes in the concentration of copper in the leachant due to the fast increase in leaching of mixed archaea compared with single archea.

Moreover qPCR (quantitative polymerase chain reaction) confirmed that adsorption promotion occurred between S. metallicus bacteria and A. brierleyi in mixed system [43].

IV. CHEMICAL PROCESSING OF SILICATES

4.1. Leaching of silicate

Eliana et al proved experimentally on leaching of metakaolin by hydrofluoric acid to dissolve aluminium and silicate. A recovery reaching to 96% was achieved under 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 reached 99% of silicon and 70% of aluminium[44].

From the results obtained, it can be concluded that alkali leaching of Kaolinitic clay is a function of concentration of the extracting agent, NaOH. It can also be inferred that the suitable concentration for extraction is 40% w/w NaOH solution which gave the highest solubility of silica leached as 65%. The amount of alumina leached by different concentrations of NaOH increased with increase in concentrations of NaOH but the solubility of alumina in the alkaline solution was less than that of silica at any specific contact time studied[45].

Jun et al studied the effect of calcinations on kaolin leaching and reported that:

The preparation of porous alumina/silica materials via selective leaching of silica or alumina from activated kaolinit resulted from the generation of metakaolin or amorphous silica along with superior acid dissolution of alumina or alkali dissolution of silica, respectively, under the appropriate activation temperatures.

1. The characterization of prepared porous materials indicates that their specific surface area (SSA) increases with increasing dissolution of alumina/silica in aqueous leaching solution from activated kaolinite. The pore volume of porous alumina decreases with increasing dissolution of silica, while there is no correlation between pore volume of porous silica and alumina dissolution of activated kaolinit. The prepared porous alumina/silica materials belong to the mesoporous materials, despite the slight change of their pore size with the dissolution of activated kaolinit.

2. When the porous alumina is obtained via alkali leaching of kaolinite activated at 1150 °C for 15 min, the SSA, pore size and pore volume are 55.8 m^2/g, 6.06 nm and 0.1455 mL/g, respectively. For the porous silica prepared via acid leaching of kaolinit activated at 850 °C for 15 min, these values are 280.3 m^2/g, 3.06 nm and 0.1945 mL/g, respectively. The adsorption tests confirm that the prepared porous alumina has a superior adsorption of Cu^{2+}, Pb^{2+} and Cd^{2+}, with maxima of 134 mg/g, 183 mg/g and 195 mg/g, respectively. However, the porous silica has difficulty adsorbing the above-mentioned heavy metal ions[46].

Direct hydrochloric acid processing of Egyptian gluconitic sandstone (Baharaiya Oasis) to produce chlorides of potassium and aluminium was achieved using a leaching autoclave as an alternative route leach processing technique.

The most favourable conditions of extraction of 95% of potassium present in gluconitic sand stone are temperature, acid concentration 20% by weight, grain size – 75µm and leaching time 90 min. A calculation of Temperature dependence of the rate constant gave an activation energy of 16.6KJ/mol which is consistent with values of activation energies reported for diffusion controlled reactions[47].

Studies on HCl acid activation of three fuller's earth consisting of smectite as the main component have shown them to be suitable for obtaining active earth's. The use of theses activated clay in refining sunflower oil was examined. Best decolorizing power of (TR) semectite was obtained by a bleaching process using 2M HCl for a short period. It supposed that this process causes an increase of the number of acid centers. Best decolorizing power of (CH) and (CR) semectite were obtained by rising concentration and duration of HCl to 4 and 6 respectively[48].

4.2. Mechanical Activation of Silicates

Ismail and others studied the mechanical activation of Kalbsha Kaolin ore and found that:

1. The Chemical composition of Kalabsha Kaolinit reveals that it is a low grade kaolinit, and mainly, composed of kaolinit, quartz and minor amount of antaze.
2. Deterioration of kaolinit structure increases with increasing grinding time and calcination temperature, whereas the destructive takes place mainly in the direction of C axis.
3. The surface area increases from 18 m^2/g of the effect original sample to reach maximum value of 42 m^2/g at 120 min grinding time, and decreases upon further grinding may be due tao the agglomeration of the individual particles.
4. The reactivity of kaolinite was increased as grinding time and calcination temperature increase. This may be attributed to the disassociation of kaolinit structure. The extraction of aluminum after 30 min. leaching time is about 97.52% for ground kaolinite at 240 min. and 85.4% for 180 min. grinding time. While the maximum of aluminum from calcinated kaolinite was 93.47% at temperature 550°C[49].

Mechanical activation is one of the most efficient pretreatment methods used to accelerate the reaction rate in the mineral carbonation technology. This paper reviews the current research related to this technique with a specific focus on three types of magnesium silicates - olivine and serpentine, and partially serpentinized olivine. First, the effects of mechanical activation on magnesium silicates are listed and compared with regard to a variety of milling conditions, including diverse energy inputs, grinding aids and mill types. Then, the existing literature determines the extents of mechanical activation, reviewed with respect to downstream carbonation processes, including direct gas/solid carbonation, direct aqueous carbonation, indirect aqueous carbonation, and indirect solid/solid mechanochemical carbonation. Finally, suggestions are made for further study on applying mechanical activation in an integrated mineral carbonation process, in order to lower the energy consumption of commercial systems[50].

4.3. Pressure Leaching of silicate Minerals

Li and others studied the pressure leaching of zinc silicate:

1) Zinc silicate ore from Guangxi province of China contains hemimorphite and smithsonite as economic minerals, and quartz and chlorite as gangue minerals. Zinc is present in three modes: associated with silica, weakly adsorbed to crystalline quartz surface and substituted isomorphously for iron in chlorite structure.
2) When the solid to liquid ratio of reaction mixture is maintained constant at 1:3 g/mL, and the mixture is agitated at a speed rate of 550 r/min, the optimum leaching conditions are ˘106 ʒm of particle size, 132 g/L of sulfuric acid, 90 min leaching at 120 ć and 1200 kPa. Under the optimum conditions, the extraction ratio of zinc is 99.25%, and the dissolution of silica is only 0.20%.
3) After leaching at the optimum conditions, the morphology and constituent phases of the residue change a lot as compared with the non-leached zinc silicate ore. The main minerals in leach residue are quartz and small amounts of undissolved oxide minerals of iron, lead and aluminum associated with quartz.

4) Sulfuric acid pressure leaching of zinc silicate ore is a viable process that effectively extracts most of zinc into solution and rejects silica from its minerals[51].

Optimum leaching conditions and final liquor composition varies according to the ore mineralogy. More fundamental studies have demonstrated that the rate of leaching and character of the residue is dependent on the level of Mg, Mn and Cr in the ore, the potential of the slurry and salinity of the process water. Early work indicates that the incorporation of chromium into alunite scale also affects the incorporation of silica and nickel and the settling of the residues. Various types of scale have been identified during different stages of leaching and possible means of minimising scale are discussed. The clay-rich nickel laterites in Western Australia differ from Moa Bay laterite in mineralogy and have comparatively high silica and low chromium content[52].

Zhenyu et al. studied the pressure leaching and found:

(1) Calcination leads to structural damage of the trace muscovite around surface, edge, interior, and cleavage planes. Destroyed sites provide larger specific area and higher chemical activity so as to reduce internal diffusion resistances of leaching agents and chemical reaction resistances. Structural damage of trace muscovite are caused by high-temperature calcination, and further developed during pressure leaching of the quartz sand using H_2SO_4 and NH_4Cl as leaching agents. The trace muscovite is dissolved and separated from quartz sand by coupling effects of calcination and fluorine-free pressure leaching.

(2) Si and K within muscovite are preferentially leached before Al during fluorine-free pressure leaching of the hydrothermal vein quartz. S–OH in H_2SO_4 reacts with the Si–O–Al structure of calcinated muscovite so as to realize a cation exchange of H^+ and Al^{3+}. The remaining active Al_2O_3 is finally dissolved when $Al_2(SO_4)_3$ enters into diffusion layer. The reason why the removal rate of Al is limited as 87.5% is that the remaining trace elements Al and Na replace Si in the quartz lattice[53].

Amer and Ibrahim made comparative study between the pressure leaching and the calcined Beryl ore and concluded that:

1. The optimum conditions of fluoride technique are 1:3 beryl: Na_2SiF_6 ratio, 800°C, 2 hours and leaching the roasted product with 20% H_2SO_4 at 90°C for one hour. At these conditions 85% of beryllium can be extracted.
2. The optimum conditions of sulphuric acid pressure leaching are: 270 °C temperature, 10 mole/liter sulphuric acid concentration, 10% solid content and 30 minutes leaching time. At these conditions 92% of beryllium can be extracted.
3. Comparing the two evaluated techniques reveal that pressure leaching has the following advantages:

1. It takes place in only one stage while the fluoride technique takes place in two stages namely, roasting followed by leaching treatment
2. Short time is needed for the reaction (30 minutes).
3. Low chemical consumption compared to fluoride technique[54].

4.4. Bioleaching of Silicate

The bioleaching mechanism 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 [55].

Grudev make experiment to indicate the release of K^+ from silicate mineral and suggests the presence of B. mucilaginous capsule consisting of exosuccharides by bacteria leads to mineral dissolution[56]. Vainberg suggested also the dissolution of metal due to the production of organic acids in culture media [57]. Also, there is a paucity in experimental data supporting this hypothesis. The present study indicates the leaching of K^+ and SiO_2 from silicate minerals 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 [58].

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 SiO_2 and O_2. The variation of concentration of SiO_2 affect the balance between two stages of metals the stage of reaction between SiO_2 and K+ which leads to mineral degradation.[59].

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 attractive method for removal of metals. The bioleaching for four months using molasses make the process uneconomic. Bioleaching needs short courses and remove about 60% at least of iron from sand quartz.

The optimization of Anthraquinone-2,6-disulfonate (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[60&61]. Several experiments were done to confirm that Bacillus species is suitable for bioleaching of quartz sand by dissolving calys and iron minerals from quartz surface [62].

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 prevents the reproduction of bacteria present during the bioleaching, the problem of acid consumption and precipitation of silica is cost effective. To overcome these problems, heap leaching and pH control of liquor should be applied [63].

Jiangman studies:

1 – The effect of bacteria known as Paenibacillus mucilaginosus BM-4, he adapted in this paper the acidity and the temperature with minerals of layer crystal structure as kaolinit and chlorite.,

2- The adsorption of Paenibacillus mucilaginosus BM-4 on bauxite and kaolinit he found that kaolinit is adsorbed electrostaticlly by bacteria Paenibacillus mucilaginosus BM-4 while bauxite is adsorbed as langmiur isotherm.,

3 – The flotation recovery of kaolinite increases 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 Paenibacillus mucilaginosus BM-4.,

4 – The flotation experiment was done on the mixture of bauxite: kaolinit with ratio 5:1 using bacteria BM-4 using modified Hallmond tube, the results indicate increasing the ratio of Al/Si from 3.05 – 8.06 and alumina recovery reachs to 83.0%.[64]

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 increases 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 helps the strains to bioleaching[65].

V. CONCLUSION

The aim of this article to give a review on the new techniques for processing of minerals in the last few decades, and also define the new directions for leaching of sulfides and silicate minerals also giving an idea about the occurance of the ores in Egypt. It also review the new technologies of sulfides minerals processing (leaching, mechanical activation, pressure leaching, and bioleaching) and silicate minerals processing (leaching and bioleaching).

The main concern in this review is 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. In leaching of pyrite, sulfur is oxidized to elemental sulfur under comparable conditions. The main direction of leaching pyrohotite unoxidized sulfide is to oxidize it to sulfur and can also be oxidized to sulfate. Due to the low solubility of Cu-sulfide, the non-oxidative 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 the 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 is 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 display dissimilar temperature dependence, suggesting that the rate-determining 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.

Leaching of silicate ores.

1. Leaching of metakaolin by hydrofluoric acid to dissolve aluminium and silicate. A recovery reaching to 96% was achieved under 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 reached 99% of silicon and 70% of aluminium.
2. Deterioration of kaolinit structure increases with increasing grinding time and calcination temperature, whereas the destructive takes place. The surface area increases from 18 m^2/g of the effect original sample to reach maximum value of 42 m^2/g at 120 min grinding time, and decreases upon further grinding may be due to the agglomeration of the individual particles. The reactivity of kaolinite was increased as grinding time and calcination temperature increase. This may be attributed to the disassociation of kaolinit structure. The extraction of aluminum after 30 min. leaching time is about 97.52% for ground kaolinite at 240 min. and 85.4% for 180 min. grinding time. Leacing of metakaolin by hydrofluoric acid in the atmospheric reaction dissolve.
3. Solid to liquid ratio of reaction mixture is maintained constant at 1:3 g/mL, and the mixture is agitated at a speed rate of 550 r/min, the optimum leaching conditions are ˘106 μm of particle size, 132 g/L of sulfuric acid, 90 min leaching at 120 ć and 1200 kPa. Under the optimum conditions, the extraction ratio of zinc is 99.25%, and the dissolution of silica is only 0.20%. After leaching at the optimum conditions, the morphology and constituent phases of the residue change a lot as compared with the non-leached zinc silicate ore. The main minerals in leach residue are quartz and small amounts of undissolved oxide minerals of iron, lead and aluminum associated with quartz. Sulfuric acid pressure leaching of zinc silicate ore is a viable process that effectively extracts most of zinc into solution and rejects silica from its minerals.
4. The release of K^+ from silicate mineral and suggests the presence of B. mucilaginous capsule consisting of exosuccharides by bacteria leads to mineral dissolution. Dissolution of metal due to the production of organic acids in culture media. 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.

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 physica1 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.

Role of CMRDI in the Leaching of Sulfides and Silicates

Leaching of silicate

(1) Leaching of Clay with Hydroflusilicic Acid [66]
(2) Production of high purity alumina from clay kalabsha [67].
(3) The Characteristics of Bentonite From Ayun Musa Area, Red Sea Coast Sinai, Egypt[68]
(4) Improvement of Rheological Properties of Egyptian Bentonitic Clay through Alkali Activation [69]
(5) Combined Thermal and Structural Study of Some Egyptian Bentonitie Clays. [70]
(6) Development of Processing Some Egyptian Gluconitic Sandstone [47]
(7) Use of Clay and Waste Flusilicic Acid For Water Purification [71]
(8) Diatomaceous deposits of Fayoum, Egypt: Characterization and Evaluation for Industrial application [72]
(9) Synthesis of Zeolite AlNa from low grade Kalabsha Kaoline [73]
(10) Utilization of Egyptian Serpentine for Chemical Industries Applications [74]
(11) Preparation of polyaluminum chlorides containing nano-Al13 from Egyptian kaolin and application in water treatment [75]
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(13) Production of Metallurgical Alumina from Local Ores, Imported Ores, and Blends from Them. Ibid, 1994. [77]
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(17) Technology transfer for acid activation of bentonite for Kafr –El Dawar Company, to produce bleaching powder for oil, 2007[81]

(18) Synthesis of Mordenite Zeolite by Sol-Gel Technique and Study their Applications in the Petroleum Field for Sulphur Removal". Funded from the Egyptian Science, Technology, Development Fund, STDF, 2009-2012. [82]

(19) Production of High purity alumina from Kalabsha Kaolin and production of Aluminium Fluoride.2017 El Nasr Intermediate Chemicals Company, Cairo University, Japan University, Atomic Authority[83].

(20) Bacterial Leaching of Complex Sulphide Ore from Akarem Area [84].

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