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Development of an innovative process for the selective recovery of metals from spent refinery catalysts

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ABSTRACT

In the present work was studied and developed the treatment of spent refinery catalysts to recovery valuable metals contained in them. It was hypothesized that, using the sulfide precipitation could be possible obtain a selective precipitation of molybdenum, nickel, vanadium and aluminium after the early solubilisation of them by leaching or bioleaching processes.

The refinery catalysts are used extensively in the hydro-treating processes for the production of clean fuels from fractions distilled from crude oil. The hydro-treating processes include the elimination of nitrogen compounds, sulphur and metals from charged of the catalytic cracking.

The metals present in the charged cause the poisoning of the catalysts reducing their activity; the catalysts deactivated are classified as solid wastes by the United States Environmental Protection Agency (USEPA). Environmental regulations and interesting amounts of strategic metals guide towards the development of new feasible and sustainable process not only to treat this waste but also to recover valuable metals such as V, Al, Ni and Mo.

The work was divided in two phases: the first phase consisted in the solubilization of spent refinery catalysts by bioleaching processes with sulphur-oxidising bacteria or leaching process by sulphuric acid. Once solubilised the spent catalysts, the metal-containing wastewater was treated by adding of sulfide source and sodium hydroxide to precipitate and recovering the four metals at different pH values (second phase). The sulfide sources used were Na_2S chemical compound and H_2S gas produced by sulfate-reducing bacteria in a lactate feed anaerobic baffled reactor. Tests were conducted to determine whether could be possible obtain the selective precipitation of all metals presents at different pH values as sulfide (molybdenum and nickel) and as hydroxide (aluminum and vanadium); the molybdenum precipitation occurred at low pH value 0.5, nickel at pH value 3.5 aluminum at pH value 4 and vanadium at pH value 6. The pH values were settled by preliminary solubility tests and preliminary chemical speciation studies conducted with *Medusa* software. The selective precipitation tests were done using two synthetic base metals solution called leach liquor and bioleach liquor (solution 1 and solution 2 respectively) simulating the typical metals concentration of liquor after an operation of leaching and bioleaching processes respectively.

About the experiments conducted using as sulfide source Na_2S, the percentages of precipitation were higher than 60% for all metals investigated (Al= 65 %; Mo= 87 %; Ni= 52 %; V= 64 %;) in the synthetic bioleaching solution (solution 2) and in the synthetic leaching solution (Al= 55 %; Mo= 75 %; Ni= 54 %; V= 67 %;) (solution1). The indices of purity of precipitates were calculated considering the total weight of metal target precipitated (for example the molybdenum at pH 0.5) on the total weight of precipitates (Mo, Ni, V, Al) at pH 0.5; in both cases of bioleaching synthetic solution and leaching synthetic solution the purity indices of molybdenum were 0.86 and 0.70 at

pH= 0.5 for leaching and bioleaching synthetic solutions respectively; while about the nickel the purity indices were 0.76 and 0.92 at pH=3 for leaching and bioleaching synthetic solutions.

Regarding the experiments conducted using as sulfide source the H_2S gas produced by anaerobic baffled reactor containing sulfate-reducing bacteria the average sulfate reduction rate in the ABR was 130 mg L^{-1} d^{-1} and the average dissolved sulfide concentration 190 mg L^{-1} mg L^{-1}. The precipitations of Mo at target pH of 0.5 was 36-72% and V precipitation was 64-70% at pH 6 depending of the initial concentrations of them. Percent Ni precipitation was up to 40 % at target pH of 3.5. The purity indices of Mo and V precipitates were 0.97 and 0.90 at pH 0.5 and pH 6, respectively. Were also conducted the technical and economic analysis processes by *Super Pro* simulating chemical process software on four processes (C-C: leaching solution-Na_2S; C-B: leaching solution- H_2S; B-C: bioleaching solution- Na_2S; B-B: bioleaching solution-H_2S) were determinate the payback time of the processes (PBT= time of return of capital invested), the production of liquid waste, the percentages of base metals recovered and the total recovery of matter. The results obtained shown that the process C-C was the best among the all factors investigated (PBT, production of liquid waste, percentages of base metals recovered and total recovery of matter). The PBT of C-C process was less than 2 years, the recovery of base metals were all higher than 80%, the total recovery of matter was around the 90% and the production of liquid waste was around 3 tons/ tons of catalysts treated.

CHAPTER ONE

INTRODUCTION

The hydro treating processes are used extensively in the oil industry for the production of clean fuels from fractions distilled from crude oil. The most important function of hydro treating is the removal of sulphur compounds (hydrodesulphurization, HDS) by reaction with hydrogen in the presence of a catalyst with the formation of hydrogen sulphide. H_2S is removed from the gas stream through a cleaning solvent and is then converted to elemental sulphur in a Claus plant. The processes of hydro treating is used for the following operations (Ullmann's, 1996):

- Removal of sulphur, nitrogen, oxygen, and arsenic from charged of the reformer (naphtha) to avoid the poisoning of platinum catalysts of the same reformers;
- increase the thermal stability of fuels used in air transport also increased the smoke point can be achieved with a partial hydrogenation of aromatic;
- Partial removal of sulphur from the distilled fractions (gas oils) to obtain a certain standard of quality mixtures used for diesel and light oils from heating. Unsaturated hydrocarbons of these fractions are hydrogenated to increase stability and reduce the chromatic tendency to coking of the cracking products;
- elimination of nitrogen compounds, sulphur and metals from charged of the catalytic cracking to reduce the deactivation catalysts (due to N_2 and metals) and to reduce the sulphur content in the cracking products;
- reducing the sulphur content of heavy fuel oil; of diolefins of pyrolysis gases (arising from the systems of ethylene production) to prevent the formation of rubber deteriorates the stability the gases themselves;
- improving the odours, colour and stability oxidation of lubricating oils using mild hydro cracking. De-aromatization and removing compounds sulphur, nitrogen and oxygen by pressure hydrogenation of oils lubricants (high-pressure hydro treating).

The catalysts for hydro treating are generally comprised of Mo deposited on a support of alumina (Al_2O_3) with Ni or Co, which increase the removal of impurities do not want such as sulphur, nitrogen and metals through processes of hydro desulfurization (HDS), hydro de-nitrogenation (HDN) and hydro de-metallization (HDM). Many of these catalysts are regenerated through processes of reactivation, usually heat, repeated several times, even as the catalytic capacity is hopelessly compromised and must therefore be replaced with virgin catalyst (Ullmann's, 1996, Coluccio, 2001).

The sulphur compounds are present as hydrogen sulfide, thiols (mercaptans), sulfides (thioethers), which cause corrosion of thiophenes equipment, odours products and poisoning catalysts. In addition, sulphur compounds in fuels give rise to emissions of SOx, so their concentration must be reduced as much as possible. This is done with processes desulphurization and conversion of H_2S to elemental sulphur, which has a some commercial value. The nitrogen compounds are more stable than sulphur and are then only partially removed during desulphurization; removal nitrogen must be made on the power to send to catalytic cracking or hydro cracking to avoid deterioration of catalysts and to lower the percentage of N_2 in fuel (NOx emissions into the atmosphere). The oxygen compounds are contained in the oil as naphthenic acids (carboxylic acids of cycloalkanes) and phenols. Since corrosive, they must be removed or distilled. Phenols cause unpleasant smell are eliminated in the catalytic cracking process. The dissolved metals cause poisoning of catalysts and then removed in a specific step ahead of de-metallization catalytic conversion processes. In the catalytic cracking process, where the accumulation of vanadium and nickel gives serious problems, using additives are added to neutralize metals (Ullmann's, 1996). The processes are characterized primarily by hydro refinement CS bond breaking, and then CO and CN elimination of sulphur, oxygen and nitrogen in the form of H_2S, H_2O and NH_3. The typical use of hydrogen from the reforming sections, possibly supplemented by hydrogen produced in an appropriate facility. Is possible to treat both the light fractions that the intermediate fractions (kerosene, diesel) for obtaining finished products conform to the specifications of the law regarding the content of sulphur; are also treated well charges to be transferred to sensitive processes sulphur or nitrogen, such as the reforming. Petroleum refining operations generate huge annual amount of catalysts. Currently, the amount of hydro-processing catalysts produced in the world is around 150000-170000 tons / year (Marafi and Stanislaus, 2008). This value is expected to increase in coming years, due to the increasing increase in the refining of heavy fractions (sands, asphalt, etc. ..) that contain high percentages of sulphur, nitrogen, asphaltenes and metals, in addition, the need to obtain fuel for automotive finest complying with environmental regulations increasingly more stringent (eg, ULS diesel, Ultra-Low Sulphur) will further increase the demand for this type of catalysts. The catalysts are classified as hazardous waste with EWC code 160802 "spent catalysts containing metals transition hazardous or dangerous transition metal compounds "and they are covered by the Decree. 152/06. Considering the intrinsic value of catalysts such, even in the current period when the price of metals is collapsed, it is unlikely that they will be land filled but, alternatively, undergoing processes pyro-metallurgical able to recover most metals content.

1.1 Hydro desulfurization process

The most important process of naphthenic oil industry is to hydro desulfurization, in which all compounds of sulfur are removed by reaction with hydrogen in the presence of a suitable catalyst. The catalysts used for hydro desulfurization processes must be able to function in the presence of H_2S, sulfur compounds and nitrogen without suffering an early poisoning. They are very selective towards desulfurization, while it is reduced to a minimum the ability to induce cracking of heavier hydrocarbons. Oxides and sulfides metals such as Co, Mo, Ni and W generally represent the active compounds. Here are ordered by activity:

- hydro desulfurization: Co-Mo> Ni-Mo> Ni-W> W-Co.
- hydrodeazotazione: Ni-Co-Ni = W> Co-Mo> Co-W.
- Saturation of olefins: Ni-W> Ni-Mo> Co-Mo> Co-W.

The most common are made up of oxides of molybdenum and cobalt (or nickel) on γ-alumina support. Sometimes the support can be composed of silica. The nickel and cobalt oxides CoO- NiO exercise promoting effect on the activity of the catalytic system MoO_3-Al_2O_3. The catalysts are usually prepared by soaking support solutions in which alumina is dissolved salts of Co and Mo, the material is calcined at 600 ° C to obtain the oxides. The properties converters are influenced not only by the method of preparation, also by the surface properties of the alumina support, especially in the case of desulfurization of heavy fractions of fixed-bed because of low diffusivity of the liquid charge. The catalyst is charged into the reactor when metals are active in the form of oxides, but the efficiency converter is maximum when they are in the form of sulphides. For this reason is subjected to an initial adding of H_2S gas to get to CoS and MoS_2 compounds that are active in catalysis. The component catalyzes the reaction is the MoS_2, activated by cobalt, which limits the sintering of the crystals. During the operation, the catalyst is gradually deactivated by the deposition of carbonaceous material (Coke) and metals, which inhibit the active sites. The tendency of hydrocarbons to form the Coke is due to their basic pH and the formation of nuclei aromatic condensed high molecular weight: they are adsorbed on the surface of the catalyst preventing contact with the fluid. To determine the activity of the catalyst, it uses the exothermic catalysis reaction, as a result of which the power output of the reactor, has a temperature higher than a few tens of degrees Celsius respect the input. The temperature is then monitored for the parameters establish the proper functioning of the catalyst: when the temperature falls below the range indicated is necessary to regenerate or replace the bed. The regeneration of the catalyst is possible only if the deposits are carbon deposits: in the case are also present the metal deposits is necessary directly replace the catalyst, as is the case with the LC-Finer given to the ORIM S.p.A. Typical temperatures which occur chemical reactions of hydro desulfurization are between 300 and 400 ° C. The regeneration involves injecting small amounts of air in the reactor, after cooling and a remediation system with nitrogen: the burning of coke is made on controlled conditions, in order to avoid excessively increases the sintering temperature resulting in the catalyst. The main operating variables affecting the process of desulphurization are: temperature, pressure, space velocity and H2/HC relationship. The space velocity is a parameter typical of the processes catalytic: it is indicated by the acronym LHSV (Liquid Hourly Space Velocity) and represents the relationship between the flow of fluid supplied (m3 / h) and the bed volume of ctz (catalyst) (m3). The Table 1 shows the typical parameters of hydro desulfurization for different hydrocarbons.

Charge	ΔT boiling	Sulfur in the product	P (bar)	T (°C)	LHSV (h-1)	Lifetime ctz (months)
Benzine	70-170	1 ppm	5 ÷8	310-360	5 ÷ 8	36-48
Kerosene	160-240	50-100 ppm	8 ÷12	310-360	4÷ 6	36-48
Light diesel	240-350	0.1-0.2%	10 ÷20	320-380	4÷ 6	36-48
Heavy diesel	300-380	0.1-0.3%	20÷30	320-380	2÷ 4	36-48

Table1 process operative condition of desulfurization for different hydrocarbons

The temperature is generally the minimum that allows create a good desulphurization, as an increase in temperature above this value would only have the effect of accelerating the coke formation and thus reduce the duration of the catalyst. The temperature the process is adjusted according to the hydrocarbon fraction input (gasoline, kerosene, naphtha, etc.). During the exercise, due to the progressive deactivation of the catalyst, is necessary increase the operating temperature of the reactor, so as to obtain a product always has the required quality specifications. The temperature is always carefully controlled, since charges rich in unsaturated cause a considerable increase in temperature due to the strong reaction of exothermic saturation.

The control pressure is made on the separator products at high pressure. The operating pressure should be as constant as possible, since a higher value promote the catalyst duration and improves performance (lower coke formation). The LHSV depends on the incoming charge, and size by catalyst granules. When operating at higher LHSV values of the design value, that is, with a range of superior power, are necessary higher operating temperatures to ensure the specific desulfurization, but these results increase the production of coke.

The hydrogen to hydrocarbon H_2/HC is defined as the ratio between the flow rate (Nm3 / h) of gas injected into the reactor and the flow (Nm3 / h) power. An increase of this ratio, at constant pressure, is translates into a reduction of the partial pressures of gaseous components and consequently in increased vaporization of the charge, in particular, it lowers the partial pressure of

H_2S that has an effect inhibitor on the rate of hydro desulfurization. Ratio values lower than the project lead to a rapid deactivation of catalyst. Because the amount of gas that can be recycled is function of compression ratio, the fraction of re- circulated gas during an operating cycle is gradually decreasing due to the increase of charge drop in reactor. This is acceptable H_2/HC until the ratio is at least equal to the value of the project, otherwise the catalyst must be regenerated or replaced. In all cases in which the relationship H_2/HC gets too low (eg. Due to heavy losses) then is necessary reduce the flow of incoming loads. It is essential that the H_2 has a certain partial pressure so that the hydrogenation reactions are complete, the report is that the H_2/HC pH2 depend on the percentage of H_2 in current circulation that turn depends on the purity of restoration (makeup gas) and amount of volatile hydrocarbons and H_2S gases that accumulate in recirculation. The amount of H_2 required to desulfurization reactions obviously depends on the hydrocarbon fraction to be treated: for kerosene, for instance, is equivalent to 0.3 kg / kg sulphur removed, while the diesel is about 0.5 kg S H_2/kg removed (Coluccio, 2001).

1.2 Process of hydro cracking

The hydro cracking process was developed to increase yields distillates having better quality than those obtained through fluid catalytic cracking. The charges subject to hydro cracking of distillates are typically coming from distillation vacuum by thermal or catalytic cracking processes or is it starved of oil asphaltenes. The operating conditions of section cracking reactor include temperatures around 400°C and pressures of 8-15 MPa. The reactions take place on a catalyst metals in the presence of hydrogen sulphide. The major advantages of this process are essentially two different products to obtain high quality industrial-scale (non-fuel oil remain residues of low quality) and extreme flexibility in regard to production, in the sense that we can maximize the yield of a particular produced at the expense of others (for example, the yield of gasoline, gasoline cherosene or gas-kerosene). Modern hydrocrackers are made two units: one unit of de-sulphurisation, and de-nitrogenation de-oxygenation with Co-Mo catalysts and a second unit of hydrocracking that using catalysts Ni-W or Ni-Mo. After fractionation of the liquid gas, naphtha and middle distillates, the product of the bottom of the fractionator is sent to the hydrocracking reactor. The residue of hydro-treating processes have been developed by major oil companies on the basis of the experience desulphurization of gasoline and middle distillates. These processes are carried out mainly in fixed-bed reactors, but with loads (0.5-2 m3 charge per m3 of catalyst). The so-called on-call rooms are often installed at the entrance of reactor as a trap for metallic impurities and solid and extend the lifetime of the reactors at HDS and HDN. This time varies from 6 to 12 months in case the pre-treatment are absent. The catalysts are typically based on Co, Mo and Ni, similar to those used in hydrogen spirits. Despite the advantage of a high yield of pure light distillates, the hydro-cracking of residue used only in a few locations in the world due to high investment and operational costs (300-400 m3 of H_2 per m3 of residue).

The fluidized bed processes are very suitable for this purpose because of the severe operating conditions associated with a rapid deactivation of catalyst. A further advantage of these processes is represented by low pressure drop in reactor. The catalysts are based both of metals particularly expensive - and therefore constantly replaced and reborn the current processes running on an industrial scale are the H-Oil (Texaco) and the LC-fining (Lummus). They use 0.5-1 kg of catalyst Ni-Mo or Co-Mo per tons of material from the fluidized bed. Another process hydro-conversion modified - known as HYCON Shell - came into function in a plant in 1989 from 4000 tons / day. This also process involves two distinct steps: the first metal content supply is reduced by 80% with a ctz-90 mounted on SiO_2; second step in the desulphurization and conversion is obtained in various fixed-bed reactors in series by catalyst Ni-Mo supported on alumina. The operating conditions (T = 400 ° C, p = 15-20 MPa) are similar to those other hydrocracking processes. Since de-metallization catalysts are turned off in a relatively short period of time, must be continually replaced, because regeneration is not possible (Ullmann's, 1996).

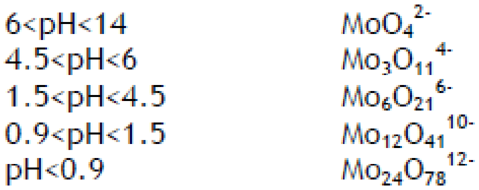
1.3 Metals in catalysts

1.3.1 Molybdenum

Molybdenum is a chemical element with a density transition quite high (10.22 g/cm3 at 20 ° C) is not found free in nature but form very stable compounds such as molybdenite MoS_2. The chemical and physical properties of the metal are given in Ullmann's, 1996. The primary minerals contain approximately 0:05 to 0:25% Mo, while secondary from 0.01 to 0.05%, by means of flotation is possible to produce concentrates containing up to 90-95% MoS_2. Generally together with molybdenite is Covellite (CuS), for which the production of Mo is always associated with copper. The most important secondary sources of Mo are obviously catalysts exhausted, where the concentrations of the metal can reach 16-18%, depending on the type of catalyst. Molybdenum trioxide MoO3 is by far the most widely used compound, especially the metallurgical industry for the production of stainless steel (Ullmann's, 1996). It 'used in special alloys with Zr, Ti, Hf, and W, and iron-molybdenum alloys (Fe-70% Mo, Fe-Ni-Mo 15%). The Mo pure metallic powder is produced from trioxide for reduction with hydrogen. Another important use is, as already stressed, in industrial catalyst, either as oxide and sulphide usually coupled with other metals (W, Ni, Fe, Co). The trioxide is a component of base from which Mo compounds such as ammonium molybdate, sodium molybdate, Mo metallic alloys Fe-Mo are produced. There are two types of MoO3 on the market: the trioxide technical Molybdenum (55-64% Mo) and the pure trioxide with higher qualification 99.5%. The technical product is used in the production of molybdates sodium and ammonium, the pure trioxide and molybdenum steels; as catalyst in the petroleum industry for the elimination of compounds sulfur, nitrogen and heavy metals, chemical industry processes oxidation of methanol to formaldehyde and benzene to cyclohexane. The trioxide is used purely for the preparation of molybdenum metal, reagents and catalysts in which requires a high degree of purity. MoO3 is reduced by hydrogen at 500-600 ° C to MoO_2 then to Mo metal between 900 and 1000 ° C. The hydrated trioxide ($MoO_3 \cdot H_2O$ or H_2MoO_4) is also known as molybdic acid. The precipitates when a H_2MoO_4 concentrated solution is treated with HCl Na_2MoO_4. Ammonium molybdate [(NH_4) $2MoO_4$] is obtained by leaching preliminary technical MoO3 with water at 75 ° C to remove impurities soluble, then after filtration, the trioxide is dissolved in hot (60-80 ° C) an excess of concentrated ammonia. Is commercially heptamolybdate the ammonium hydrate [(NH_4) $6Mo_7O_{24} \cdot 4H_2O$]. The ferric molybdate [$5MoO_3 \cdot Fe_2O_3$] is mainly used for preparation of necessary catalyst selective oxidation of methanol to formaldehyde. Sodium molybdate [Na_2MoO_4] is obtained by dissolving MoO_3 in sodium hydroxide concentrated at 50-70 ° C after removing the impurities with a leaching into the water. It is used for the production of pigments and as a flame retardant. The molybdenum pentachloride [$MoCl_5$] is the most important among halides of molybdenum. It consists of dark green crystals-blacks and obtained by oxidation of Mo metal of chlorine in the atmosphere. It is catalyst used as in some particular reactions (Friedel-Crafts) as well as a coating of iron and steel. The esacarbonile molybdenum [$Mo\ (CO)_6$] is the first compound on the production of all organic compounds of Mo.

The organic compounds of Mo and its complex organic-sulfur compounds present a big raise interest in biochemistry and in applications where it is necessary to reduce friction between moving mechanical parts (Ullmann's, 1996).The chemistry of molybdenum in aqueous solution is rather complex. In particular, it exists in aqueous solution with different ionic forms, depending on the pH and redox potential of the solution. In specifically, the Mo^{3+} forms complexes hydrochloric and oxalic; the MO^{4+} cyanide forms complexes, while there are complex hydrochloric cyanide, and phosphate of Mo^{5+}. The MO^{6+} form instead several complexes, both organic and inorganic phosphorus ions, arsenic, vanadium, fluoride, citric, oxalic, tartaric, etc. A thorough discussion of the thermodynamic equilibrium of the complex of molybdenum in aqueous solution is reported in the text Pourbaix, 1974. The cation Mo^{3+} is stable in a strongly acid-reducing agent; once oxidized, it slowly transforms into a red compound whose composition is still poorly understood. Trioxide, MoO_3, composed widely used in industry, is presents instead of white colour.

The Mo^{5+} is characterized by a typical deep blue (hence the famous blue molybdenum), the typical colour of the solution is given by the ion $Mo_2O_4^{2\ +}$, known as hydrated molybdenite $Mo_2O_5 \bullet 3H_2O$.Mo hexavalent compounds are undoubtedly the most important, specifically, depending on the pH, the following complexes are stable:



$6<pH<14$	MoO_4^{2-}
$4.5<pH<6$	$Mo_3O_{11}^{4-}$
$1.5<pH<4.5$	$Mo_6O_{21}^{6-}$
$0.9<pH<1.5$	$Mo_{12}O_{41}^{10-}$
$pH<0.9$	$Mo_{24}O_{78}^{12-}$

1.3.2 Nickel

Nickel is a silvery-white element of the typical metallic properties. The commercial importance of nickel closely related to its ability to form with other elements, alloys characterized by high hardness, stiffness and strength corrosion in a wide temperature range; for this reason it is of fundamental importance in the iron and steel. It has a relative density equal to 8.9 and other interesting physical properties, while the chemical properties are very similar to those of iron, copper and cobalt. The main minerals which sulphides are extracted [NiS, Ni_3S_2, Ni_2FeS_4, (Ni, Fe) 9S8], arsenide [Niassa, Nias], silicates [(Ni, Mg) $6Si_4O_{10}(OH)_8$]. Unfortunately despite the Nickel is more abundant than zinc, lead and copper in the earth's crust there are only a few deposits commercially significant. More than 90% of nickel sulphide concentrates in the world are treated by pyro-metallurgical (600-700 ° C); this treatment includes three unit operations: roasting, smelting and converting. In the first step sulphur is removed as part of the SO2 in the flue and the iron is oxidized. During the second step the product is melted roast in the presence of a silica matrix that is combined with the oxidized iron and produces two immiscible phases, a slag silicate liquid that is discarded and a solution of molten sulphides containing metals of interest. In the operation of converting the remaining sulphur is oxidized to sulphur dioxide, iron is oxidized completely and melted for remove the silicate slag: a concentration remains high purity nickel and copper sulphides. Several industrial processes have currently in operation for the treatment of concentrated Ni, Cu, such as those employed by Falconbridge, Inco, Sumitomo and Outokumpu (Ullmann's, 1996). In a typical hydrometallurgical process, the concentrate is leached with sulphuric acid or hydrochloric acid to dissolve Ni and Cu, while the sulphides are oxidized to elemental sulphur or insoluble sulphates soluble. Often, the leaching is conducted in two steps according to a counter current scheme to operate a first neutralization of the solution. The copper is removed by cementation, so it gets a solution containing sulfate or chloride leaching of nickel and a solid residue rich in copper, which is treated in a pressure leaching or roasting / leaching to solubilize the copper sulphate and recovery by electrolysis. Nickel is recovered from the solution as a metal for electroplating or by reduction with hydrogen. If in the mineral base is also present the cobalt is necessary to perform a solvent extraction, as Ni and Co have very similar chemical properties. Nickel is mainly used in ferrous alloys, stainless steels, alloys for special purposes (eg. space materials) and treatments plating. Chemicals are used as the nickel catalysts in hydrogen in the refining of vegetable oils and oil heavy, as pigments in plastics, glass and ceramics in the bathrooms electroplating and production of rechargeable batteries (Ullmann's, 1996). The most important nickel chemicals are:

- Nickel carbonate - $2NiCO_3•3Ni(OH)_2•4H_2O$ - is the compound more important industry, although there is the carbonate that the hexa-hydrate and anhydrous. It is insoluble in water but becomes soluble with acid with release of CO_2. When heated to temperatures above 450°C giving a decomposition of nickel oxide with high surface area specific. The commercial nickel carbonate is obtained by precipitation from a solution of Na_2CO_3 and $NiSO_4$; the composition that is obtained depends on the temperature and the purity of the solution. It is used in pH regulation in galvanic baths, the production of catalysts and some pigments and other nickel compounds.

- Nickel hydroxide - $Ni(OH)_2$ - usually precipitated from a solution a nickel salt treated with NaOH or KOH (green precipitate gel). The conditions of precipitation obviously affect on the physical characteristics of the product. Heated to 250 ° C gives NiO, is soluble in acid but not in the water, while ammonia gives the formation of a complex amino blue. It is used as an active component in catalysts, but the main use in the positive electrodes of Ni-Cd.

- Nitrate of nickel - $Ni(NO_3)_2•6H_2O$ - produced by dissolving Ni metal in nitric acid. The reaction is vigorous and emissions must be strictly controlled. Nitrate is obtained by precipitation of hexa-hydrate from which is very difficult to produce the anhydrous. The hexa-hydrate is then the one used commercially for the production of ctz (impregnating the carrier with an aqueous solution of $Ni(NO_3)_2• 6H_2O$) or for the production of $Ni(OH)_2$.

- Nickel Oxide - NiO - is green and is found in nature as Bunsenite. The nickel oxide can adsorbed on the surface oxygen atoms to give high ratios: Ni. So there seems to be the only black oxide Ni_2O_3 as consisting of NiO surface. It is quite refractory and slowly dissolves in acid. It is produced by calcination of other Ni compounds such as nitrate, oxalate or hydroxide at 1000 ° C. The black

oxide, soluble, is obtained by calcining the carbonate Ni at 550 ° C. Both can be reduced by H_2 to Ni metal. The NiO is used in the production of ceramic glazes and catalyst and in the glass industry.
• Nickel sulfate - $NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$ - available commercially in the two hydrated forms: the blue-green hexahydrate, which contains 22.3% Ni and crystallized from solution between 30.7 and 53.8 ° C and which contains the green hepta-hydrate 20.9% Ni and crystallizes below 30.7 ° C. Sulfate is also produced by dissolving Ni or NiO in H_2SO_4. This salt is usually used as the electrolyte in electroplating baths. It is also used as starting material for the production of other Ni compounds. Other important compounds are Ni sulfide NiS, the Ni tetrafluoroborate (BF4) 2 •6 H2O, tetracarbonyl Ni $(CO)_4$, oxalate Ni $(COO)_2 \cdot 2H_2O$, acetate, Ni $(CH_3COO)_2 \cdot 4H_2O$, Ni formate $(HCOO)_2 \cdot 2H_2O$.

1.3.3 Vanadium

Vanadium forms several minerals (roscoelite, Montrose, carnotite, corvus, vanadite, descoizite) and usually it is located in sulfides form. Oxides and silicates together with other elements as Pb, Fe, Ti, Ba, U, Cu, Zn, Si and alkali metals. Vanadium is proceeds mainly as a secondary product of titan magnetite processing (production of Ti and Fe), bauxite (Al), uranium and petroleum refining. The world's largest producers, considering both the primary extraction and secondary recovery (eg. By catalysts and ash) are South Africa, China, Russia and the United States. The main material from which is possible to get the primary vanadium is the slag that is obtained from the treatment of titan magnetite: from roasting of these materials before in a rotary kiln with addition of coal and then in a electric arc furnace is obtained a slag containing Fe-V having a concentration of V 25% (as V_2O_5). The slag is ground and calcined at 750-850°C in presence of an alkali metal to form vanadates soluble, for example sodium. By addition of H_2SO_4 and a ammonia salt is possible to precipitate the polyvanadate/ammonium metavanadate, that for calcinations gives the pentoxide V2O5 (Ullmann's, 1996). Acid leaching is also used for processing minerals and slag containing vanadium, although the purification of the solution leaching is more laborious and takes several steps. Vanadium, is derived from primary minerals by flotation: the float, containing V is separated from the gangue and mixed with soda ash or other compounds; after that it proceed with hot water leaching and subsequently ammonium precipitation.

The mixed pyro-hydrometallurgical processes are those more employees, especially in the recycling of spent refinery ctz (sulfuric acid production and refining petroleum products), filter cakes and boiler ashes. Vanadium metal is not produced by electrolysis but for reduction of the pentoxide by carbon, hydrogen and aluminum. Most of the vanadium produced is currently used for steel production (85%), non-ferrous alloys (9%), chemical industry (4%), other (2%). Small percentages of vanadium improve the elasticity and resistance to high temperature of carbon steels. The non-ferrous alloys in which is used vanadium are represented mainly by those containing titanium and nickel super alloys for the aerospace industry. The V_2O_5 is the most important compound of the vanadium: is prepared for thermal decomposition at 500-600°C of poly/metavanadate ammonium in oxidizing air of atmosphere and is used primarily as ctz (catalyst) for the production of sulfuric acid to lower the point of fusion of enamels for glass and ceramics, as an inhibitor of corrosion and as a starting material for the production of other compounds (red phosphors in cathode ray tube screens, pigments, etc…). The V_20_3 trioxide is used as an alternative to the pentoxide in alloys Fe-V and in the production of cathodes of lithium batteries, both primary and minor. The most important salts of vanadium are vanadil-sulfate ($VOSO_4 \bullet 5H_2O$) with the typical blue color used in alternative to the pentoxide for the production of ctz, VOC_2O_4, $VOCl_3$, nitrides and carbides of vanadium (Ullmann’s, 1996). The chemistry of vanadium aqueous solution is similar to molybdenum and therefore very complex, since it can form anions and cations depending on the Eh and pH values of solution (Pourbaix, 1974).

1.3.4 Aluminum

Aluminum is the most abundant metallic element in the land crust, is generally combine d with other elements and is very rare to find in pure state. The main ore from which extracts the aluminum is bauxite, an impure hydrated oxide containing 48-64% and the rest of Al_2O_3, SiO_2, Fe_2O_3, TiO_2 and CaO. The bauxite deposits are quite extensive and there are virtually on all continents, except apparently in the Antarctic. The metallurgy of aluminum is carried out in two stages: first, it extracts the pure alumina from bauxite by wet process, while the second gives the pure through an electrolytic process. For the production of alumina from primary minerals there are various processes designed for this purpose, such as those deville-Pechiney, Peniakoff and Bayer, only chemicals and Pedersen, Haglund and Serpek in which the chemical step is preceded by a melting bauxite treatment in an electric furnace for obtaining iron-alloy and a slag rich in aluminum treated later by a hydrometallurgical process. However, now, the bayer process is almost exclusively applied in the world (Hugony, 1968). Regarding the second phase, the electrolytic process most widely used in industry for the production of aluminum is the Hall-Heroult, this process involves essentially two main steps: leaching with cryolite (hexa-fluoroaluminate trisodium, NA3AlF6) for the dissolution of alumina and electrolysis of molten salts. In The bayer process the bauxite previously calcined is finely wet ground and then leached using special mills with NAOH to give sodium aluminate $NaAlO_2$; removed the contaminants from the solution (Si and P from insoluble compounds and other metals precipitated by pH), causes the hydrolysis of aluminum up to get the aluminum hydrate, which is obtained alumina by calcinations. The conditions depend on the type of leaching bauxite, include temperatures between 100 and 250°C and concentrations of NaOH to 2.5-6 moles/liter. The precipitation of aluminum occur after the filtration and cooling of the pregnant solution, where are add a few grains of Al(OH)3: in this way the precipitation of hydroxide is obtained. The latter compound is then calcined at temperatures above 1100°C to extract the alumina content of at least 99.5% (Impurities consisting of Fe_2O_3, Na_2O, SiO_2) (Ullmann's 1996). In the Hall-Heroult process, the alumina is placed a bath of cryolite (5% solution of Al_2O_3) and then subjected to electrolysis cells or electrolytic furnaces, where the solution is heated to 950-1000°C due to joule effect by electrical current flowing in the bath itself. The anode is composed of many bars of petroleum coke in which is inserted conductive metal cores, while the cathode consists of a crushed coal. The aluminum, which reduces to cathode, being heavier than the molten salt mixture forms liquid at the bottom of the cell, while on the anode oxygen is developed. The output current varies between 85 and 90%, while the power consumption is quite high, being around to 14-15 KWh/Kg of the product (Hugony, 1968, Ullmann's, 1966). Some chemical and physical properties depend on the aluminum purity; many applications of Al alloys are due to its properties, such as low density, high electrical and thermal conductivity, excellent corrosion resistance and good mechanical properties. Al alloys are very strong and can easily be produced with typical thermal processes of the steel industry. Pure Al is in fact quite flexible and has not particular strength: it is used particularly in the electrical industry, thanks to the excellent electrical conductivity (high and medium voltage cables) and the chemical industry for high resistance to corrosion when coated with a thin compact oxide layer (heat exchangers, pipes). The light alloys are widely used in the construction of mechanical parts of automobiles or other media, as well as in building for the attractive appearance of color. Aluminum is melted in alloy with Cu, Si and Mg respectively which represent the characteristic elements of the alloy construction, foundry and resistant to corrosion. Although the zinc is added in light alloys for particular uses; with the Fe forms special steels and cast, with the nickel is used for produce magnets. The alumina then is essential for the production of cement and refractories as bricks for kilns; the aluminum association made a classification that specifies the characteristics of various types of alloy (cast, machined and hardened) for which are used three different nomenclatures (Aluminum association, 2009).

1.3.5 Market trends in metal prices

The main interest of the companies that make withdrawal of oil industries ctz lies mainly in the recovery of metals value as V, Ni, Co and Mo; in recent years, however, also grew the interest in recovering of aluminum both in the form of alumina or other compounds. Most of ctz used in other refinery activity has a support of alumina (alkylation, the Claus process or removal of chlorides), which until a few years ago was simply disposed of in special landfills. But today the volume of alumina produced each years by the oil industry is enormous and landfill is no longer environmentally sustainable, if we consider that the production of primary aluminum from ore is energetically expensive, recycling of aluminum has the double advantage of reducing the energy needed to produce and conserve resources natural.

According to a forecast of Silvy (2004), the efficiency of refining capacity in the oil industry should grow by 2.4% per year, but there is a certain discrepancy between the efficiency and refining capacity. Regarding efficiency, the quantity and the type of ctz play a key role, but the demand for ctz hydro-processing to increase constantly, about 4% per year for the hydro-treating ctz and up to 8% for hydro-cracking ctz. Taking into account these considerations, the cost of those ctz could exceed of 10 and 30 U.S. $ / kg respectively.

It is remarkable that the payment to refineries by companies such as ORIM SpA for the withdrawal of ctz depends not only on the concentration of metals but also by the price on world markets. In the case of LC-Finer, the ORIM pays to the refinery approximately € 500 / tons to ctz withdraw, after the advent of the economic crisis (October-November 2008) is that the refinery pays the same amount to the ORIM, as a result of drop in metal prices on international markets. Figure 1.1 shows the prices trend of some compounds of Ni, Mo, V and Co of interest from October 2005 to May 2009 (London Metal Exchange, 2009; Metal Pages, 2009). The collapse prices in November 2008, is obvious, from May to June 2009 seems to be witnessing a slow climb, though the positive trend is often interrupted by temporary down prices. The purity of the compounds in the figure are as follows: V_2O_5 98 %; alloy Fe-V 80% V 57% MoO_3 Mo, Ni 99.8% min, 99.3% Co min. The trend of aluminum prices (99.5%) is shown in Figure 1.1.

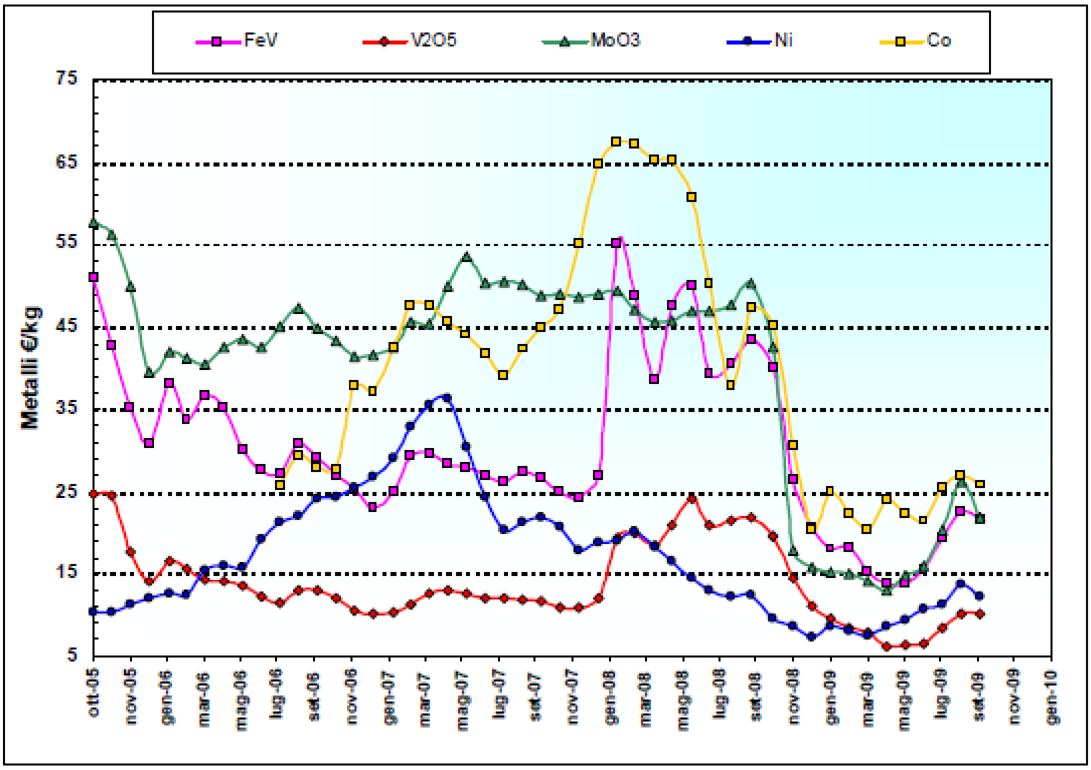


Figure 1.1 Heavy metals trends prices

The explosion in demand for molybdenum may result from international maritime regulations, which require the decommissioning by 2010, all tankers built before of 1987; another factor that might increase the price of molybdenum shortage of supply, once the crisis.

Economic begin to resolve, is the construction of new pipelines. The price of molybdenum (as oxide) increased abruptly in mid-2002, leveling off around 12 U.S. $ / kg in 2003. The temporary closure of some mines in China has pushed the price above 16 U.S. $ / kg. According to a study by Price Waterhouse Coopers, the net proceeds of molybdenum showed the highest growth in 2004 (+209%). During this period, the average price has risen from 14 to almost 40 U.S. $ / kg. In 2005, however, the price of MoO3 stood with some fluctuations, at around 70 U.S. $ / kg, while between May 2007 and October 2008 the price has remained more or less constant over 60 U.S. $ / kg (Marafi and Stanislaus, 2008).

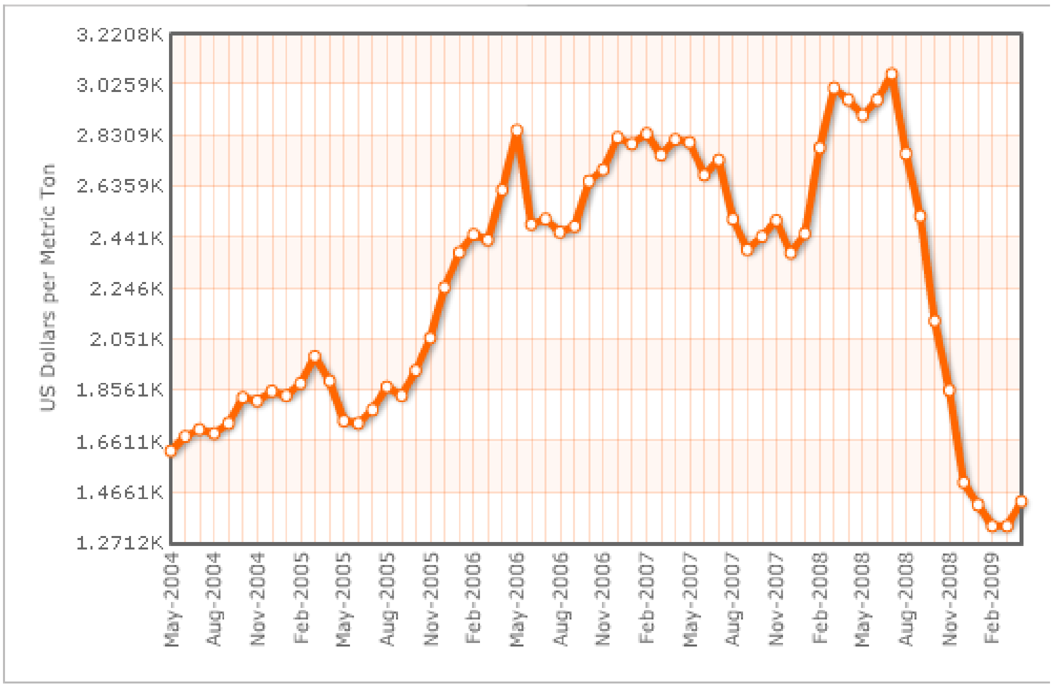


Fig 2.1 Aluminum price trend

The cobalt price has been relatively stable until the 70s, then, because of uncertainties in the supply, the price rose more than 80 U.S. $ / kg. After an initial stabilization in the 80s (about 20U.S. $ / kg) the price began to rise again in the early 90s due to the unstable political and social situation of some countries producers, to about 60 U.S. $ / kg. From 1996 to 2000, prices have always fluctuated between 25 and 45 U.S. $ / kg (Marafi and Stanislaus, 2008). The price of vanadium, however, has always shown wide fluctuations arcs in a fairly short time, because its use is linked to many sectors of the economy. Compared to 2003, in 2004 there was a increase in the consumption of vanadium of 13%, while in the previous period the consumption had increased only 2% per annum. At the end of 2005 began a slow descent that led to a stabilization prices in 2006-2007, due to the large quantities of vanadium placed on the market from China. In 2007 the prices of alloys Fe-V were around 33 U.S. $ / kg of vanadium (Marafi and Stanislaus, 2008). As for the price of nickel, it has fluctuated very similar to those of other metals. In 2005 began a continued prices growth that has reached peak (~ 35 € / kg) to April 2007, and then begin a slow descent interrupted by some short period of increases. The sharp price increase that was recorded for almost two years was due not only to an increase in real demand but also a strong speculation of investment funds that have invested heavily in commodities. The aluminum peak price was reached in August 2008 when needed for a kilogram of aluminum about 3.1 U.S. $. In the next months instead there was a subsequent free fall that has brought the price to 1.3 U.S. $ / kg. From June 2009 implemented a lift that has led the price of around 2 € / kg. It just because of these values that the aluminum recovery has never been attractive to companies that make recycling of spent catalysts (Marafi and

Stanislaus, 2008). Alumina is the heavier weight fraction of a catalyst (up to 70%). And therefore desirable that the recovery of alumina takes increase not only to avoid landfill but also to avoid the consumption of large amounts of energy, with both environmental and economic benefits. If they were also counted environmental benefits of the recovery as a by-product of the alumina ctz of recycling would certainly sustainable; currently the price at which the alumina is traded is around 600 U.S. $ / ton (Marafi and Stanislaus, 2008).

1.4 Sulfate Reducing bacteria, SRB

The sulfate reducers (sulfate Reducing bacteria, SRB) have proved very useful in the treatment of water contaminated by heavy metals and sulphates due to the characteristics of their metabolism.
This is a class of microorganisms that leads the dissimilation sulfate reduction: In this process the sulfate ion acts as an oxidizing agent for the dissimilation of organic matter, respiration of oxygen in the same way conventional. Microorganisms assimilate a small part of the reduced sulfur, but most of it is released into the environment as a sulfide ion, usually in the form of hydrogen sulfide (H_2S). The process can also be called "sulfate-breathing".
The SRB are all strictly anaerobic, and use for their growth sulfate ions, but they can also use sulfite, thiosulfate and tetrathionate(Postgate,1984).
In the absence of sulfate some sulfate reducers are strains of bacteria capable of fermentative growth if they have available an appropriate carbon source, such as pyruvate, fumarate or the sick; these bacteria simply cannot grow using oxygen as electron acceptor since this gas inhibits them.
The sulfate is a much less favorable electron acceptor is molecular oxygen of nitrate. In any case, its redox potential is sufficient to produce ATP when using a donor of electrons from NADH or FADH which is produced. Just because of the potentially less favorable, organizations using sulfate have a yield much lower than the growth of organisms that use oxygen or nitrate, compared with standard aerobic microorganisms grow relatively slowly, but are widespread and have the ability to survive in different environments and to adapt to any natural environment of our planet, but the most common: a normal aerobic environment (Postgate, 1984).
Sulfate reducing bacteria play an important role in the geological and biological cycle in the cycle of sulfur. In the latter (Fig.3.1) the SRB reduce sulfate (SO_4^{2-}) to sulfide (S^{2-}) thus providing the substrate for the oxidative sulfur bacteria, via the elemental sulfur, re-converts the sulfide to sulfate. Sulfate reduction in the assimilation of sulfate sulfur passes through the level of oxidation of

sulfides and is incorporated into an amino acid (RSH) to become the first microbial protein. The sulfur is part of the cycle through the food chain and decay of dead organisms.

Sulfate reducing bacteria are present in soil, freshwater, marine and brackish water, in hot springs and thermal areas, in oil and natural gas in deposits of sulfur in the sediments of estuaries, sewage, in rumen of sheep and in the gut of insects.

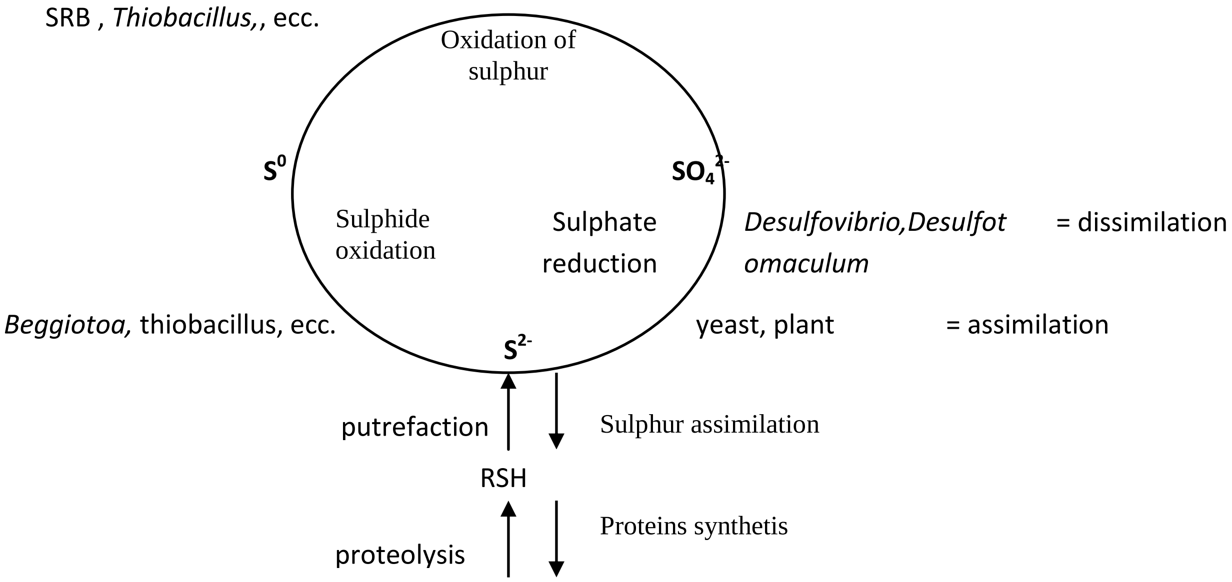


Fig 3.1 Sulfur biological cycle

The most common and popular are the SRB *Desulfovibrio* and *Desulfatomacula* (Fig.4.1), the former are most popular, mainly because they are easier to isolate.

The mesophilic *Desulfovibrio* are generally (with maximum temperatures of 45 to 48 °C), arehalophilic and do not form spores, most of them have a curved shape and tend to become filamentous. In contrast, mesophilic or thermophilic *Desulfatomacula* may be, tend to take form spores and spiral forms. Both genera are Gram-negative and prone topolymorphism in old cultures or environments are not completely satisfactory. Most *Desulfatomacula* has many flagella, while *Desulfovibrio* are fitted with a single flagellum, although known some of them without flagella.

a) b)

Fig 4.1 *desulfiovibrio* a) *desulfatomaculum* b)

1.4.1 Sulfate reducing bacteria metabolism

Metabolism consists essentially of anabolic (biosynthesis) and catabolic process. In aerobic the metabolism can be divided into three stages, as shown in Figure 5.1:

1. The breaking of the carbon substrate, an essentially anaerobic process, during which a small amount of ATP can be generated and, most importantly, during which primary electron donor are reduced to the electron transport chain (usually NAD or NADP,flavoproteins at times);
2. The transport of electrons, which is also an anaerobic process, which implies an efficient generation of ATP (phosphorylated respiration);
3. The reduction of oxygen to OH^- by the cytochrome oxidase, is a reaction that is very aerobic (final stage).

Many facultative anaerobes may omit stages of transport of electrons and oxygen reduction by relying on their energy balance only on the level of phosphorylation of the substrate; from this point of view the facultative anaerobes resemble to obligate anaerobes fermentative.

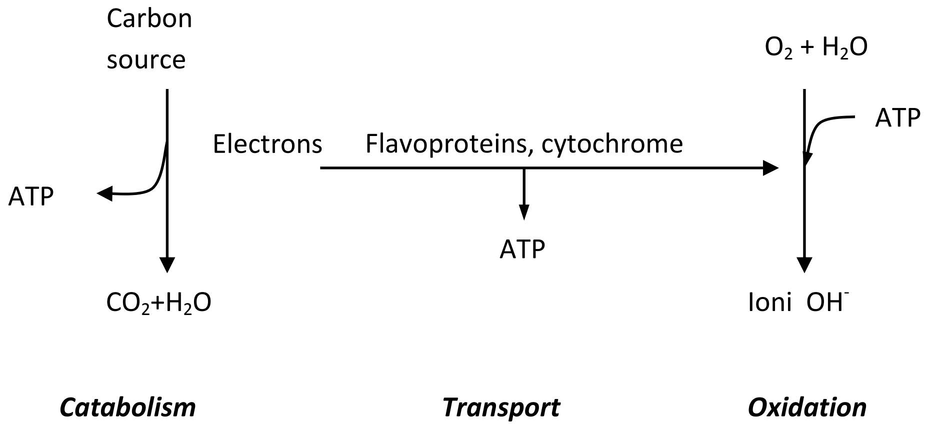


Fig 5.1 Diagram of anaerobic respiration

The sulfate reduction done by SRB is essentially an oxidative metabolism (Fig.6.1); is similar to aerobic respiration, but carbon catabolism is interrupted at the level of oxidation of acetate and oxidative stage involves the removal of oxygen atoms by sulfate and its reduction to sulfide with consumption of ATP (Postgate, 1984).

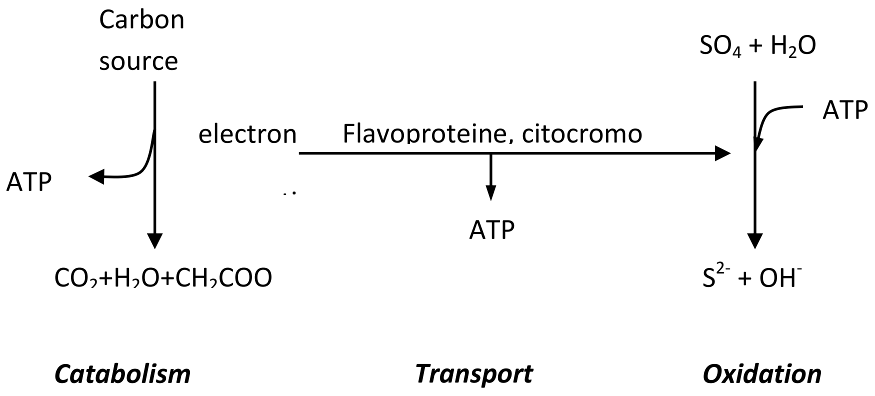


Figure 6.1 Diagram of the reduction of sulfate (dissimilation)

In addition to carbon substrates, including hydrogen gas can act as a donor of electrons to the electron transport chain, a reaction that occurs in the aerobic microorganisms, except in certain specialized bacteria, called hydrogen bacteria.

Catabolism of carbon

As already mentioned, the sulfate reducing bacteria (SRB) are strictly anaerobic microorganisms that use for their growth sulfate ions as oxidizing agents or as electron acceptors. They can grow both heterotrophic using small organic molecules that hold the dual role of electron donor and carbon source and autotrophic using H_2 as electron donor and CO_2 as a carbon source. The knowledge of the catabolic processes of SRB is somewhat fragmentary. The group of substrates used as carbon sources for growth is rather limited: some low molecular weight substrates such as lactate, formate, acetate, propionate, butyrate, some simple alcohols such as ethanol, glycerol and methanol, and hydrogen. The hydrocarbons are probably not used by the SRB. The lactate, pyruvate, glycerol, ethanol and acids of the tricarboxylic acid cycle are all oxidized to acetate and CO2. Despite the acetate can be incorporated, as a result of mixotrophy assimilation, its further oxidation coupled to sulfate reduction does not occur. Alcohols such as methanol, propanol, butanol, etc.., are metabolized to the corresponding fatty acids (propionic acid, butyric acid) and mixotrophy substrates are often "incomplete". As mentioned above, these substrates, as well as hydrogen, are "incomplete", does not involve themselves the growth of the organism, but they can support the reduction of sulfate and produce energy that the body can be used to digest organic material and then grow. With these substrates is therefore always required the presence of an additional carbon source, such as yeast extract. Figure 7.1 shows the effect of yeast extract on the growth of SRB.

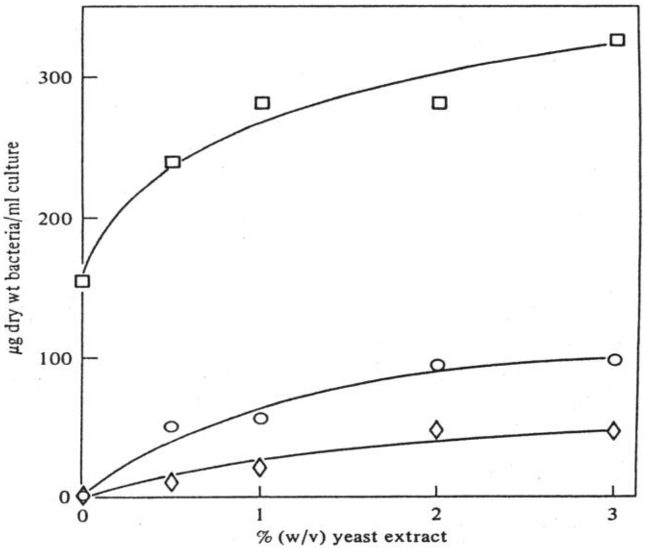


Figure 7.1 Effect of yeast extract on the growth of *Desulfovibrio*. □ lactate; O Oxamate; ◊ yeast extract.

This type of microbial nutrition characterized from chemiotrophy reactions by energy providers coupled to a process of assimilation is called mixotrophy and represents a sort of partial autotrophy. Chemiotrophy assimilation reactions of *Desulfovibrio* using hydrogen were the first example of mixotrophy to be discovered (Postgate, 1984).C1 compounds such as methanol or formate, and C2 derivatives such as oxalate and oxamate , can be completely metabolized to CO2, despite the growth yields are very low and despite not being certain that they are "complete" substrates.

According to some authors there is a terminal carbon cycle metabolism in *Desulfovibrio*: the *D. desulfuricans* coupled the oxidation processes such as the patient by the fumarase (the enzyme that leads to the reversible hydration of fumarate to malate), the reduction of fumarate to succinate and a cycle linked to the reduction of sulfate.

Succinate and fumarate accumulating transiently during oxidation of the malate and fumarate can act as a substitute acceptor of electrons, replacing the sulfate for the oxidation of hydrogen or lactate. The fumarate reduced to succinate. Catalytic concentrations of fumarate (or other intermediates such as pyruvate or lactate) accelerate the reduction of sulfate into hydrogen. Pyruvate plays a central role in the metabolism of these bacteria. Lactate is oxidized via pyruvate to acetate. Sulfate-reducing bacteria all have a system in which pyruvic phosphorus clastic , in the absence of sulfate, pyruvate is transformed into acetyl phosphate, carbon dioxide and hydrogen with a reaction stimulated by ATP.

In certain species of *Desulfovibrio* and degradation of pyruvate *Desulfatomaculum* gives bacteria a chance to grow without sulfate similar to that in the absence of O_2 has an aerobic optional, and may thus have a survival value for various species in sulfate deficient environments.

At the same cells, which develop with a low performance relative to other bacteria, the end products of oxidation of carbon substrates coupled to the reduction of sulfate acetate, water and, usually, carbon dioxide, lipids and hydrocarbons are produced less.

Catabolism of sulfur

While aerobic reduce oxygen to water, the SRB reduces sulfates to sulfides consuming water more ATP; in the absence of sulfate can be used, even if more slowly, other sulfur-containing substrates (thiosulfate, dithionate, tritionato and tetrathionate). Since the system has a sulfate reducer structural specificity, it is competitively inhibited by structural homologues of sulfate ion, in particular, selenate and mono fluoro phosphate ions are competitive inhibitors of the specific sulfate reduction, but not the reduction of ions such as sulfites or thiosulphates; chrome , perchlorate and etil-sulfate are no specific inhibitors of growth. The first stage of the dissimilation reduction of sulfate is the activation of the sulfate ion by its conversion to adenosine fosfo-sulfate (APS), a molecule in which two of the ATP phosphate residues are replaced by a group sulfate (Fig 8.1).

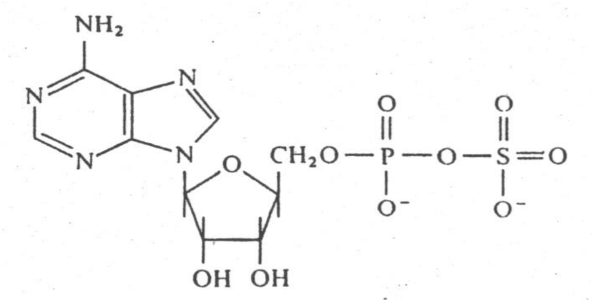


Figure 8.1 APS Structure

The sulfate ions are accumulated outside the cell by a process that is competitively inhibited by selenite. After passing through the cell barrier sulfate ions react with ATP to form adenosine fosfo-sulfate (APS) plus pyrophosphate (PP), through the action of the enzyme ATP-solforilasi (also called sulfate adenyl transferase):

$ATP + SO_4^{2-} \rightarrow APS + PP$

The constant equilibrium of ATP-solforilasi is not conducive to the formation of APS, so the reaction is "pushed" to the right, towards the products, a inorganic pyrophosphatase, which hydrolyses pyrophosphate to inorganic phosphate (P).

This enzyme in SRB has the property of being activated by reducing agents, and the organism will act when the environment is aerobic. So the bacteria can keep ATP (preventing its conversion to APS) under conditions where, for other reasons, there cannot be growth.

After activation of the sulfate is reduced, thanks to the enzyme APS-reductase (oradenylyl-sulfate reductase), adenosine fosfosulfate (APS) to sulphite than AMP with a reversible reaction:

+2e

$$\text{APS} \leftrightarrow \text{AMP} + SO_3^{2-}$$

-2e

The sulfide is dehydrated to meta-bisulfide, which is reduced as intermediate (ion dithionate, $S_2O_4^{2-}$) to give tritionato ($S_3O_6^{2-}$). -). The latter is cleaved reductively to give some to regenerate thiosulfate and sulfite; thiosulfate is reduced to give the other sulfite and sulfide, which is expelled from the cell usually as sulfides FeS or other heavy metals may be present in the culture medium. Figure 9.1 shown the diagram of the dissimilation sulfate reduction.

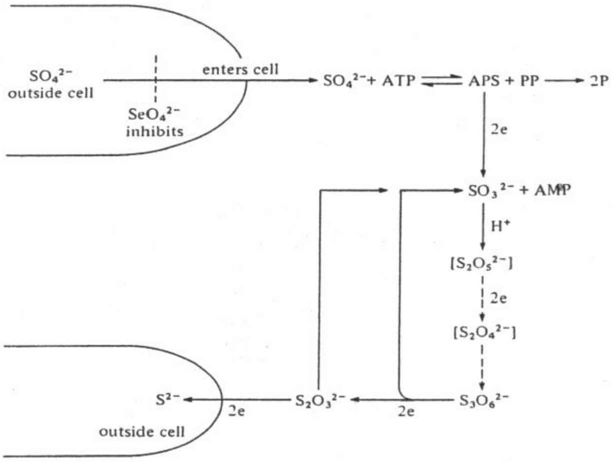


Figure 9.1 Dissimilation sulfate reduction scheme

1.4.2 Use of sulfate-reducing bacteria in the treatment of AMD and recovery of heavy metals

Recently sulfate-reducing bacteria were used for the treatment of acid waters and mine waters contaminated by heavy metals (Foucher et al., 2001). With regard to AMD, their use improves the quality of waters causing the reduction of sulfate, the precipitation of heavy metals and increase pH. The process is based on the biological production of hydrogen sulfide (equation 1) by sulfate reducing bacteria, on the precipitation of metal sulfides (equation 2) and the neutralization of the alkalinity produced by microbial metabolism (equation 3) :

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^- \qquad (1)$$

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+ \qquad (2)$$

$$HCO_3^- + H^+ \rightarrow CO_2(g) + H_2O \qquad (3)$$

where CH_2O = generic electrons donor

Acid effluents containing heavy metals and sulphates (AMD) typically have low concentrations of organic substances, which is why it is often necessary to promote the biological production of hydrogen sulfide, add a carbon source and an electron donor for sulfate reduction. Regarding the treatment of water containing heavy metals only, the process is essentially the same. In this case, so that the sulfate-reduction takes place, in addition to providing the electron donor must also provide the addition of sulfates; in the next paragraph is the thorough removal of heavy metals by the use of sulfate reducing bacteria.

1.4.3 Bioreactors for sulfate reduction

The literature shows different types of biological reactors for sulfate reduction (Hulshoffet al., 2001, Lens et al. 2001; Kaksonen and Puhakka, 2007):

- Batch Reactors;
- SBR, sequencing batch reactors;
- complete mixing reactors (CSTR, continuously stirred tank reactor);
- Anaerobic filters;
- FBR, fluidized-bed reactor;
- gas-lift reactors;
- UASBR reactor (Up flow anaerobic sludge blanket reactor);
- anaerobic hybrid reactors;
- Anaerobic contact processes;
- Membrane Bioreactors.

In Table 2.1 are reported the various reactors with their advantages and disadvantages.

Reactors	**Advantages (+) and disadvantages (-)**
CSTR	+ Regular, reliable and rapid equilibration - Low retention time of biomass
Anaerobic contact process	+ Biomass Retention time higher than of the CSTR
Anaerobic filters	+ Low shear stress + Biomass retention time higher than of the CSTR + Ability to use gravity in down flow mode + Efficient stripping of ‘H2S in down flow mode - Possible channeling the flow - The pressure gradients may be high
Fluidized- bed reactor (FBR)	+ High surface area for biofilm formation due to the fluidized carrier material + High biomass retention in the carrier + Efficient mass transfer + Small pressure gradients + No channeling the flow + Influent diluted concentrations due to flow recirculation + No clogging + Select by microorganisms with low values of Km + Ability to recover the solids from the bottom of the reactor in a down flow mode - Energy required for fluidization of the carrier - The shear stress can remove biomass - Less volume available for biomass compared to the UASB reactor due to the inert carrier
gas-lift reactor	+ Efficient mixing and mass transfer - High pressure drop of water that needs to be won when you provide

	the substrate gas
UASB reactor	+ No channeling the flow + No compaction of the mud + No cost due to carrier + No clogging + Ability to obtain high-speed processing - Release of biomass during the stopping process - Susceptible to changes in the quality of the influential
Hybrid anaerobic reactor	+ Improved retention of biomass compared to the UASB reactor
Membrane reactor	+Advanced biomass retention compared to other suspension bioreactors + Can prevent direct contact of SRB with toxic discharges - Subject to the fouling of the membrane (fouling)

Table 2.1 Different types of biological reactor for sulfate reduction

1.4.4 Sulfur oxidizing bacteria

The sulfur-oxidizing bacteria are rod-shaped, Gram-negative and no sporulation, and they also have a single polar flagellum. They can grow as adherent cells on the surface of the mineral (thanks to the production of exopolysaccharides membrane that allows the anchor to the mineral) or as planktonic cells; in this case may also form small chains of two or three cells. These bacteria are:

1.Chemolitotrophic: the energy for their growth and their maintenance is derived from the oxidation of sulfur or iron.
2. Autotrophic: use as a source of carbon dioxide.
3. Aerobes: use oxygen as an electron acceptor. In any case it can grow in anoxic, using iron (III) as electron acceptor and S (0) as electron donor.
4. Mesophilic: grows in a range of temperatures ranging from 20 ° to 40 ° C with an

optimum around 33 ° C.

5. Acidophilus: grow in a pH range 1.5 to 6.0 with an optimum between pH 2 and 2.5.

Among the most important is the desulphurization of sources and flows of natural gas and the metal bioleaching. Regarding the first point, we can say that hydrogen sulfide is a very dangerous contaminant often found in sources of natural gas. Up to this point have been developed different chemical and physical techniques for its removal. Compared to these techniques the use of microbiologicalprocesses can operateatroomtemperature andatmospheric pressure demolishing most of the installation costs. The bioleaching is a process that allows the extraction of metals from ores using the action of microorganisms.

The bacteria used in this process, especially when the concentration of metals in the minerals is low, making traditional methods of leaching inconvenient. In particular, the extraction of metals from sulfide ores is mainly based on the use of *thiobacillus* that convert insoluble sulfides soluble sulfates. The solubilization of metals can occur through a direct mechanism (adherent cells to the mineral) or indirect (cell suspensions). In the direct mechanism, the mineral sulfur (pyrite in this case) is oxidized according to the reactions:

$$4FeS + 14O_2 + 4H_2O \xrightarrow{bacteria} 4Fe^{2+} + 8SO_4^{\ 2-} + 8H^+ \qquad (1)$$

$$4Fe^{2+} + 6SO_4^{\ 2-} + O_2 + 4H^+ \xrightarrow{bacteria} 4Fe^{3+} + 6SO_4^{\ 2-} + \qquad (2)$$

that can be generalized in the form:

$$MeS + 2O_2 \xrightarrow{bacteria} Me^{2+} + SO_4^{\ 2-} \qquad (3)$$

Of course, the bacterial cells do not adhere over the entire surface of the mineral, but tend to stick close to the crystal imperfections and solubilization of metals occurs due to electrochemical interactions.

The cells found in suspension instead of acting on the mineral producing a leaching agent that chemically oxidizes the sulfur present. In this indirect mechanism, the leaching agent produced by the cells is the ferric ion acting on the rock according to this reaction:

$$MeS + 2Fe^{3+} + 3SO_4^{2-} \rightarrow Me^{2+} + 2Fe^{2+} + 3SO_4^{2} \tag{4}$$

In this process the bacteria do not require direct contact with the mineral but play only a catalytic function that accelerates the reoxidation of iron II to iron III that in abiotic leaching is 105-106 times slower. The production of Iron III is due to *Thiobacillus ferrooxidans,* a Gram-negative γ-Proteobacteria non-sporulating, rod-shaped and sized 0.5-0.6 µm wide and 1-2µm in length, in which the energy for growth and maintenance resulting from the oxidation of iron (II) or by sulfurous compounds reduced. *Thiobacillus thiooxidans* are also necessary because they can oxidize sulfur produced by reaction (4) generating sulfuric acid:

$$2S° + 3O_2 + 2H_2O \xrightarrow{Thiobacill} 4H^+ + 2SO_4 \tag{5}$$

Keep the acid environment is very important because pH above 5 you have the precipitation of iron. Although the two processes, direct and indirect, occurring at the same time, the indirect one is the most efficient.

1.5 Leaching

During the leaching, the ore, reduced to tiny size, is brought into contact with a solvent, which must be able to bring the metal in solution useful, separating it from the gangue. The chemical attack can be done with acid or alkaline solutions:

1) Water for water-soluble compounds (eg copper sulfate);
2) sulfuric acid, hydrochloric acid, nitric acid and sodium hydroxide, for oxides of metal;
3) complexing agents such as cyanide (gold and silver) or ammonia (copper and nickel);
4) reduction or oxidation of the ore through the use of gas (for example, manganese dioxide with sulfur dioxide);
5) acid-base reactions (eg the removal of the complex of tungsten at high pH values).

When the primary leaching is not responding, perform the preliminary treatment such as a grinding and then the treatment of filter-press, an oxidizing roasting or the use of bacteria to specific action (bioleaching).

1.6 Bioleaching

The bioleaching is the 'extraction of metals from ores or sulfide concentrates by using of components that are easily found in the environment. These components are mainly:
1) Water;
2) Air;
3) Microorganisms.

In chemical terms the process can be described best as a ferric leach, the reoxidation of the ferrous iron back to ferric, with the microorganisms involved as catalysts. Elemental sulfur is often a byproduct of bioleaching and microorganisms are responsible for the oxidation to sulfuric acid. The metabolism of microorganisms is based on the oxidation of ferrous iron, sulfur oxidation and the setting of carbon dioxide. Figure 10.1 shows an example of the bioleaching sphalerite (blende).

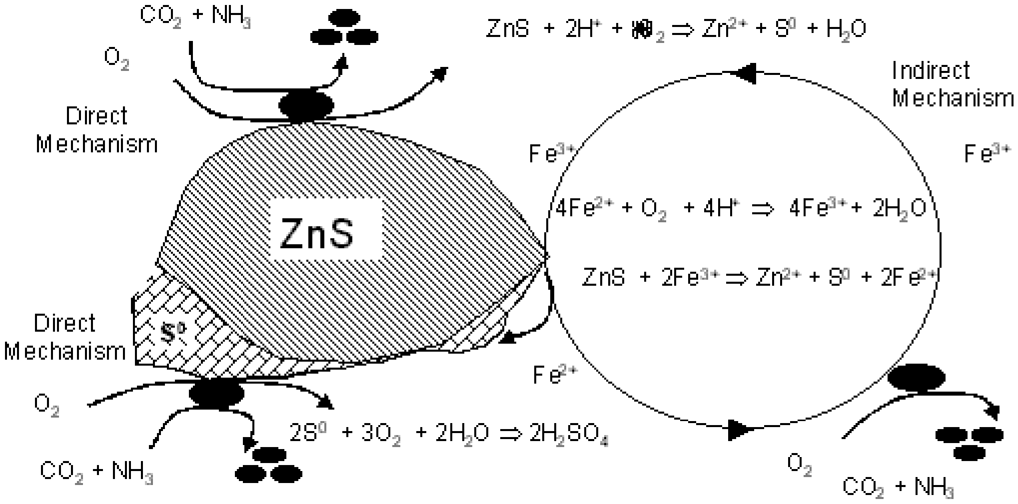


Figure 10.1 Bioleaching of Spharelite.

The bioleaching occurs naturally when microorganisms alter slowly sulfide ore bodies.

When this happens microorganisms are considered an unwanted phenomenon (think of the acid drainage leaking from the deposit to content sub marginal mines - AMD). However, once limited to a processing plant, this natural process and often unwanted, can be exploited and used for the extraction of metals from ores or concentrates sulfide. The bioleaching allows to win the refractory of minerals.

The minerals are called refractory when a significant portion of the metal contained in them can not be recovered by the simple extraction, or if the metal in question is "stuck" with other minerals ore elements such as sulfide and sulfur, or when is present coal elementary.

The bioleaching can be used to obtain metals from low resources. It is a clean technology that requires little energy and lower costs when compared to conventional thermal methods.

Initially it was believed that the bioleaching of metals from ores was mediated only by chemical reactions involving water and air, but later it turned out the involvement of bacteria as catalysts for the oxidation of metals and training.

CHAPTER TWO

STATE OF ART

2.1 Recovery processes

The recovery processes of Mo, V, Ni and Co from spent catalysts of petrochemical industry is mainly based on leaching basic or acidic chlorination, bioleaching or roasting with soda or soda ash. Very often the ctz undergo pre-treatment of heat nature acts to remove large amounts of sulfur and carbon contained in them: in the case of wet ctz must also eliminate liquid hydrocarbons (diesel, gasoline or other) of which are tinted. Other contains water so wet during the unloading of columns. Eventually there is also a step of grinding in as the yield of leaching increases with finer grain sizes.

Marafi and Stanislaus (2008) have published a review of technologies for recovery of metals from spent catalysts. It includes both laboratory-scale studies and patented processes; also gives a brief description of the main processes used on industrial scale, which of course are not available process details. Zeng and Cheng published a second review, divided into two parts, in 2009. These studies showed that all industrial processes operate a thermal pretreatment to remove coke, fuel oil and sulfur and possibly get so oxides Mo, Ni, Co and V. After that make a roasting in the presence of a salt of an alkali metal (usually soda or soda ash) or a leaching basic, almost always with soda.

This will form salts of Mo and V (Na_2MoO_4 and $NaVO_3$) soluble in water or solutions alkaline: this makes for a separation of metals already in the leaching (Ni and Co are soluble only in acidic conditions, while the Al, being amphoteric, it is only partially soluble in alkaline pH) and their recovery by precipitation or liquid-liquid extraction, is therefore easier. The main companies involved in the recovery of ctz are: Gulf Chemical and Metallurgical Corporation (USA), CRI-MET (USA), Taiyo Mining and Industrial Co. (Japan), Eurecat (France), Spent Catalyst Recycling (Germany),Aura Metallurgic (Germany), Sadaci (Belgium), FullYield Industries (Taiwan), Metallurg Vanadium (USA), Nippon Metal Tech Catalyst Cycle Co. (Japan), Moxba-Metrex (Netherlands), and Jing-Quanzhou Tai Industry Co.(China).

2.2 Literature

The article by Park et al. (2006a) deals with the recovery selective molybdenum from spent catalysts by means of carbonate sodium and hydrogen peroxide and subsequent adsorption on activated carbon active. The leaching process can be described by the following reaction:

$MoS_2 + H_2O_2 + 4O_2 \rightarrow 3Na_2CO_3 + Na_2MoO_4 + 2Na_2SO_4 + H_2O + 3CO_2$ (2.1)

The oxidant oxidizes the sulfide to sulfur and molybdenum bearing metal at its peak stage of oxidation and oxidation of the same time the carbon and fuel oil to carbon dioxide and the present water. The role of the carbonate is free to react with the molybdenum form of sodium molybdate and neutralize the sulfur dioxide produced during the oxidation to sodium sulfate. Once brought to solution, the molybdenum is adsorbed on activated carbon and then desorbed with a solution of hydroxide ammonium, and then be precipitated as ammonium molybdate transformed into molybdenum trioxide by calcination. Simultaneously with the molybdenum during leaching occurs the dissolution of aluminum, influenced by the concentration of carbonate and oxidant. Adsorption on activated carbon is, however, influenced by pH, the percentage of activated charcoal and by the time contact, while the desorption is affected by the concentration of activated carbon and the ammonium hydroxide. It shows a simplified diagram of the process:

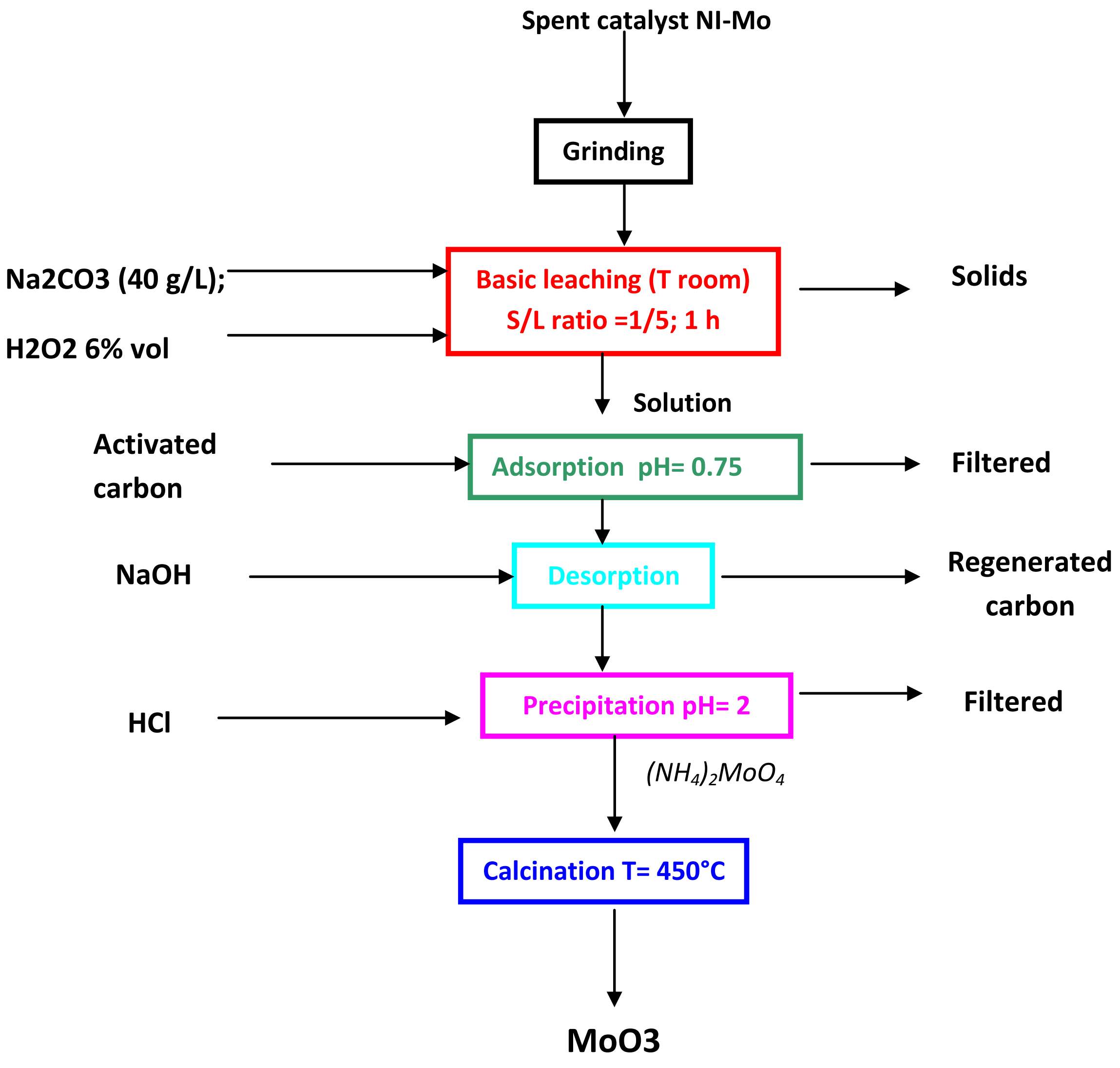


Figure 1.2. Process for the recovery of Mo proposed by Park et al. 2006a.

The study by Chen et al. (2006a) concerns the extraction of molybdenum and vanadium by catalytic residue that comes from ammonia leaching, by roasting with sodium carbonate (Na_2CO_3) and subsequent leaching with water. The dissolution depends on the roasting temperature, time and the amount of carbonate added. The two metals are then concentrated by extraction with an organic solvent (N235) and then stripped with a 10% solution of ammonia. At this point, the vanadium is precipitated as ammonium metavanadate (NH_4VO_3), adding ammonium nitrate, and molybdenum as ammonium polymolibdate ((NH_4) $2MoO_4$) bringing the pH to acidic values with the addition of HNO_3.Both precipitates are subjected to calcination to obtain MoO_3 and V_2O_5. Before of the recovery of the two metals is necessary to eliminate the phosphorous and arsenic impurities with the addition of magnesium nitrate $Mg\ (NO_3)\ _2$ and ammonia. The precipitation is strongly influenced by pH of initial solution and the reaction time, and is described by following reactions:

$$HPO_4^{2-} + NH_4^{+} + Mg^{2+} \rightarrow MgNH_4PO_4\downarrow + H^{+} \tag{2.9}$$

$$HAsO_4^{2-} + NH_4^{+} + Mg^{2+} \rightarrow MgNH_4AsO_4\downarrow + H^{+} \tag{2.10}$$

To achieve a greater purity of the molybdenum trioxide can make an evaporative crystallization bringing the polymolibdate ammonium in solution.

The process scheme is shown in Fig 2.2.

The research group of Prof. Chen has also developed another process that provides a roasting basic with NaOH at 750 ° C for 30 minutes can form vanadate and sodium molybdate (Chen et al. 2006b). These compounds are dissolved in the subsequent leaching with water at 80 ° C. The solid residue of leaching, containing nickel, cobalt and aluminum are most subject to leaching acid (H_2SO_4) at 80 ° C by means of which is possible retrieve a concentration of Ni-Co. The basic solution is instead processed with barium hydroxide $Ba\ (OH)_2$ which allows the precipitation of $Ba_3\ (VO_4)_2$, while the molybdenum is recovered as $BaMoO_4$. The spent solution is then added CO_2 in the precipitation of $Al\ (OH)_3$ from which you can obtaining alumina calcination at 1200 ° C.

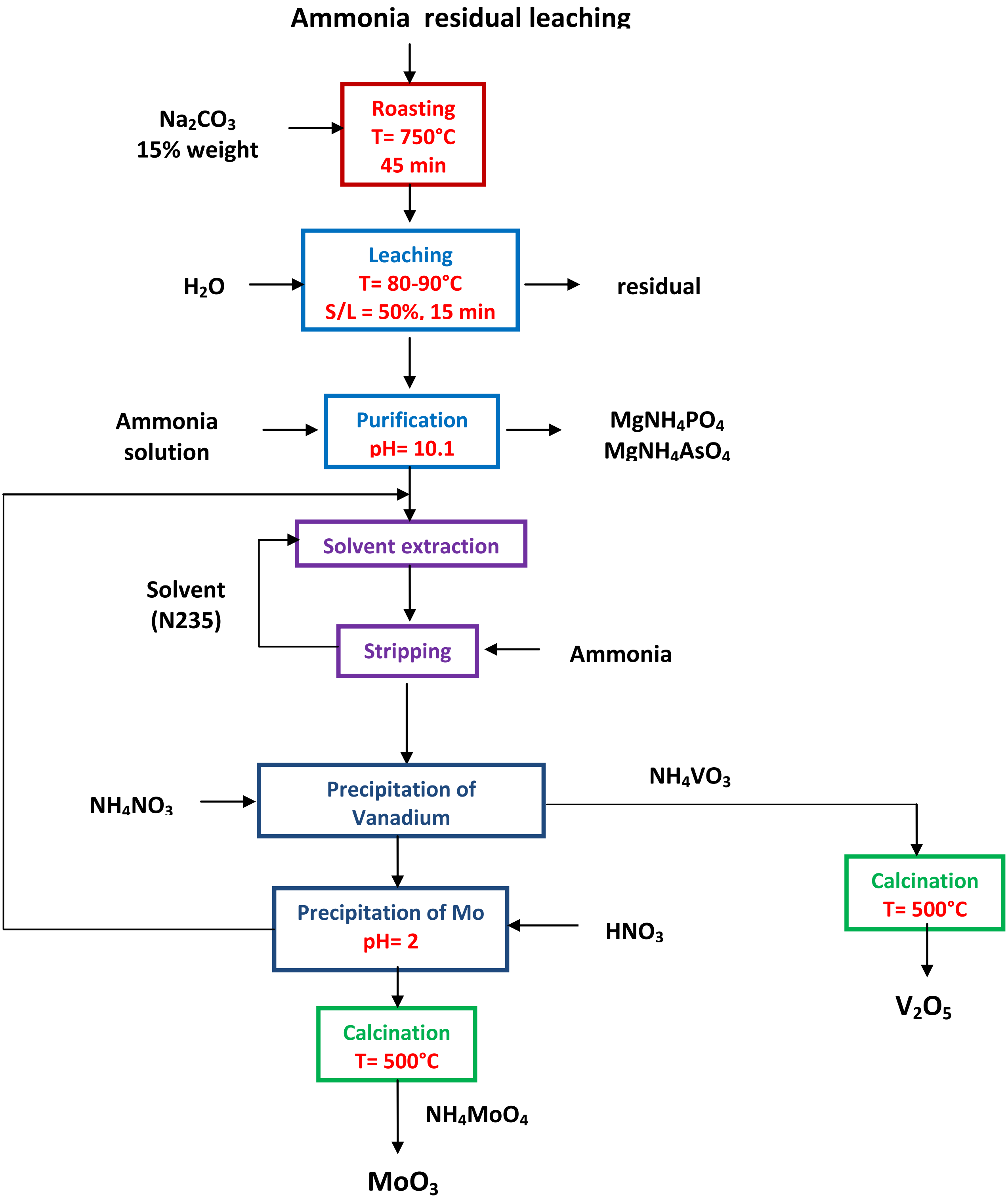


Figure 2.2 - Process for recycling of catalysts (Chen et al., 2006a)

The study of Park et al. (2006b) reports a hydrometallurgical process for the recovery of molybdenum trioxide (MoO_3) from spent catalysts through the use of Na_2CO_3 and H_2O_2. The efficiency of dissolution in stage of leaching is affected by the solid-liquid ratio and it decreases when the ratio increase. It also depends on the concentration of Na_2CO_3, H_2O_2 and the percentage of pulp. The leaching process can be represented by the following reactions:

$$MoS_2 + 2H_2O_2 + 3.5\ O_2 \rightarrow MoO_3 + 2H_2SO_4 \qquad (2.11)$$
$$MoO_3 + Na_2CO_3 \rightarrow Na_2MoO_4 + CO_2 \qquad (2.12)$$
$$2H_2SO_4 + 2Na_2CO_3 \rightarrow 2Na_2SO_4 + 2CO_2 + 2H_2O \qquad (2.13)$$

The amount of impurities (Al, Ni, P, Si, V) in the solution leaching depends on the concentration of carbonate and water peroxide. Obtained the solution containing molybdenum, it can be processed in different ways to recover the metal as calcium or ammonium molybdate, molybdic acid or trioxide molybdenum. In this study, it is recovered in the form of molybdate ammonium, as shown by the reactions below.

$$Na_2MoO_4 + 8HCl \rightarrow MoCl_6 + 2NaCl + 4H_2O \qquad (2.14)$$
$$MoCl_6 + 8NH_4OH \rightarrow (NH_4)_2MoO_4 + 6NH_4Cl + 4H_2O \qquad (2.15)$$

The process scheme is shown in Figure 3.2 Kar et al. (2004) studied the recovery of molybdenum from catalysts after several reactivations. The extraction consists of a first roasting, and later with Na_2CO_3 leaching with water bring Mo in solution as sodium molybdate (Na_2MoO_4). Finally, the metal can be recovered by precipitation as molybdate or ammonium at pH 2, or if greater purity is required for adsorption onto activated carbon, as shown in the block diagram in Fig 4.2. The polyimolibdate ammonium can be obtained by roasting at 450 ° C for MoO_3. The study examines the roasting time, temperature (450-700 ° C) and the amount of Soda ash addition. The same Kar has published a similar study the following year (Kar et al., 2005).

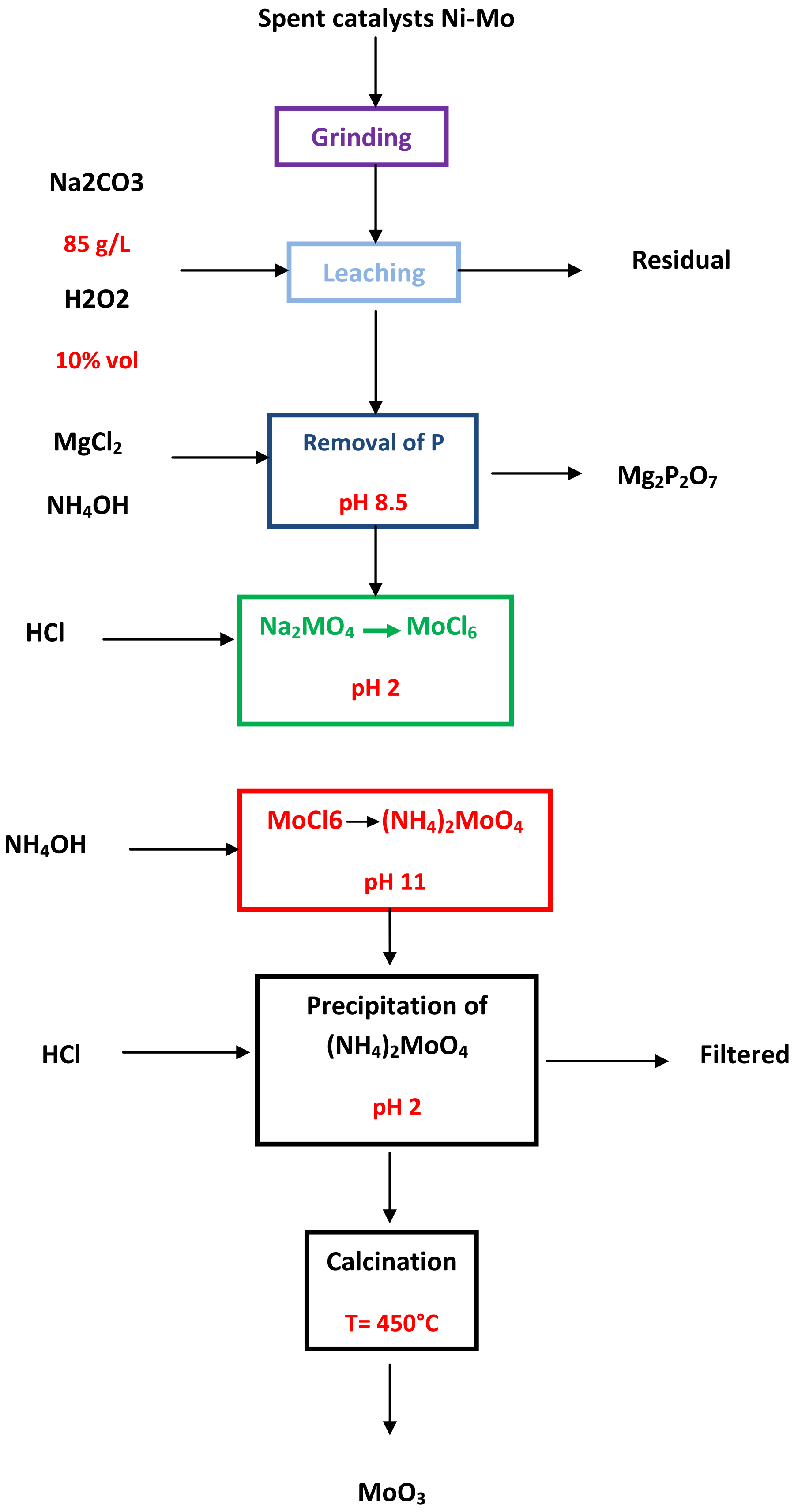


Figure 3.2 - Process for recycling of Ni-Mo ctz (Park et al., 2006b).

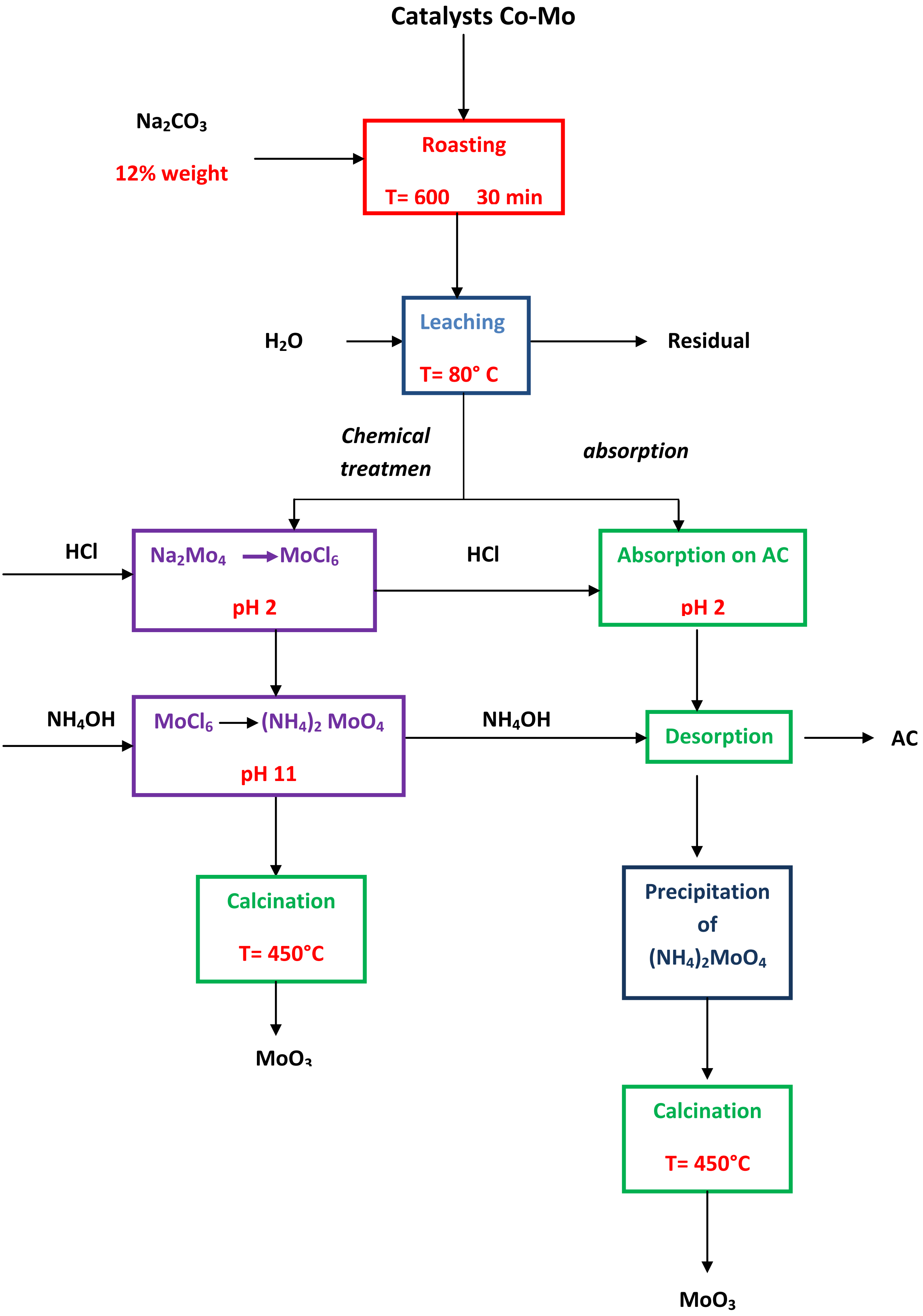


Figure 4.2- Process of recovering metals from ctz Co-Mo (Kar et al., 2004).

Zhang et al. (1996) investigated the solvent extraction of molybdenum and vanadium from a solution of sulfuric acid (pH 1.5) in presence of other metals such as Al, Co, Ni and Fe. Vanadium and molybdenum are simultaneously extracted with LIX 63 dissolved in Exxsol D80.Once extracted, the V (IV) is selectively stripped from the organic phase for using 2M sulfuric acid, while the Mo (VI) is removed with a aqueous solution with 10% ammonia. The extraction of metals is strongly influenced by pH: pH less than 2 V and Mo are selectively extracted from other metals present in solution. The recovery of molybdenum by ion exchange was investigated by Kononov et al. (2003): various ion exchange resins were tested to extract the Mo, which is later stripped by 15% ammonia solution. The process, of course, is strongly influenced by pH, since the Mo oxidation state changes and then can be either as anion or as cation. The balances are following, from pH <1 (left) to pH> 10 (right):

$$MoO_2^{2+} \leftrightarrow Mo_8O_{26}^{4-} \leftrightarrow Mo_7O_{24}^{6-} \leftrightarrow MoO_4^{2-} \qquad (2.16)$$

The article of Busnardo et al. (2007) concerns the treatment of catalysts, which is Ni-Mo Mo-Co. The recovery of metals is carried out through a calcination of dried and ground ctz in the presence of $KHSO_4$ at 350-600 ° C in a flow of air in order to avoid the reduction of sulphates to sulphides or SO2. The reactions that occur during calcination are:

$$NiO + 2KHSO_4 \rightarrow NiSO_4 + K_2SO_4 + H_2O \qquad (2.17)$$

$$CoO + 2KHSO_4 \rightarrow CoSO_4 + K_2SO_4 + H_2O \qquad (2.18)$$

$$Al_2O_3 + 6KHSO_4 \rightarrow Al_2(SO)_4 + 3K_2SO_4 + 3H_2O \qquad (2.19)$$

$$MoO_3 + 2KHSO_4 \rightarrow MoO_2SO_4 + K_2SO_4 + H_2O \qquad (2.20)$$

Cobalt and nickel are precipitated as hydroxides by adding NaOH and bringing the pH to 12. Aluminum is precipitated at pH 7-8 instead with the addition of sulfuric acid. The molybdenum is recovered through solvent extraction (MIBK) and subsequent crystallization of eptamolibdate ammonium $(NH_4)\ 7Mo_6O_{24} \cdot 4H_2O$.

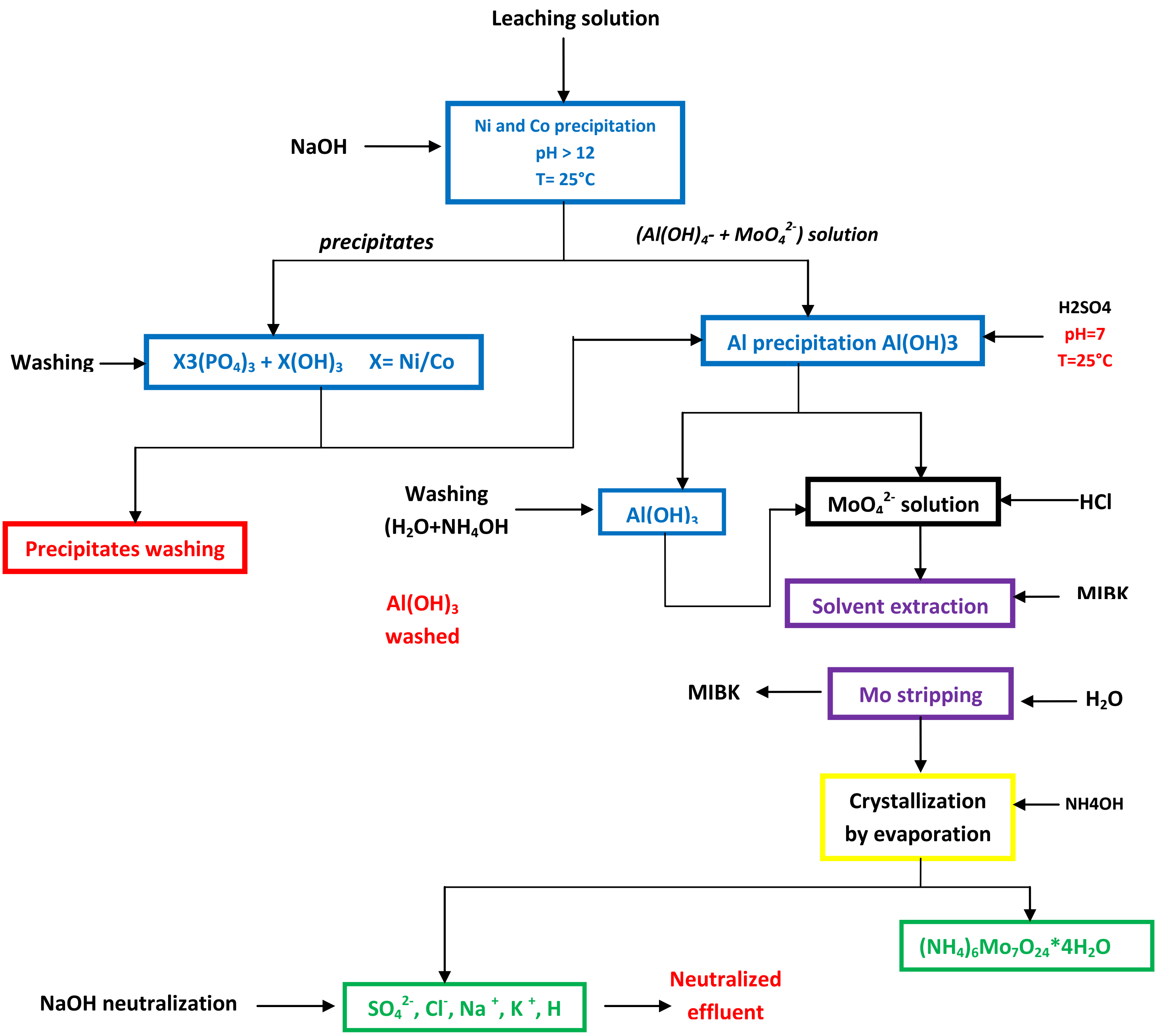


Figure 5.2. Process of recovering metals from ctz Ni-Mo-Mo and Co (Busnardo etal., 2007).

Navarro et al. (2007) studied the recovery of vanadium from oil fly ashes by leaching and subsequent selective precipitation of the metal. The leaching is conducted with sodium hydroxide being more selective sodium carbonate and sulfuric acid extraction of vanadium; recovery is then performed using precipitation. The article also examined the extraction solvent as an alternative to the precipitation (the most suitable solvent turns out to be the ALIQUAT 336) and the possibility of the leaching with H_2SO_4 or Na_2CO_3. It shows a summary diagram of the process and a brief description of it. Despite the high efficiency of the leaching acid for vanadium, the authors believe it is preferable to use a alkaline leaching that dissolves Ni and Fe present in quantities not negligible.

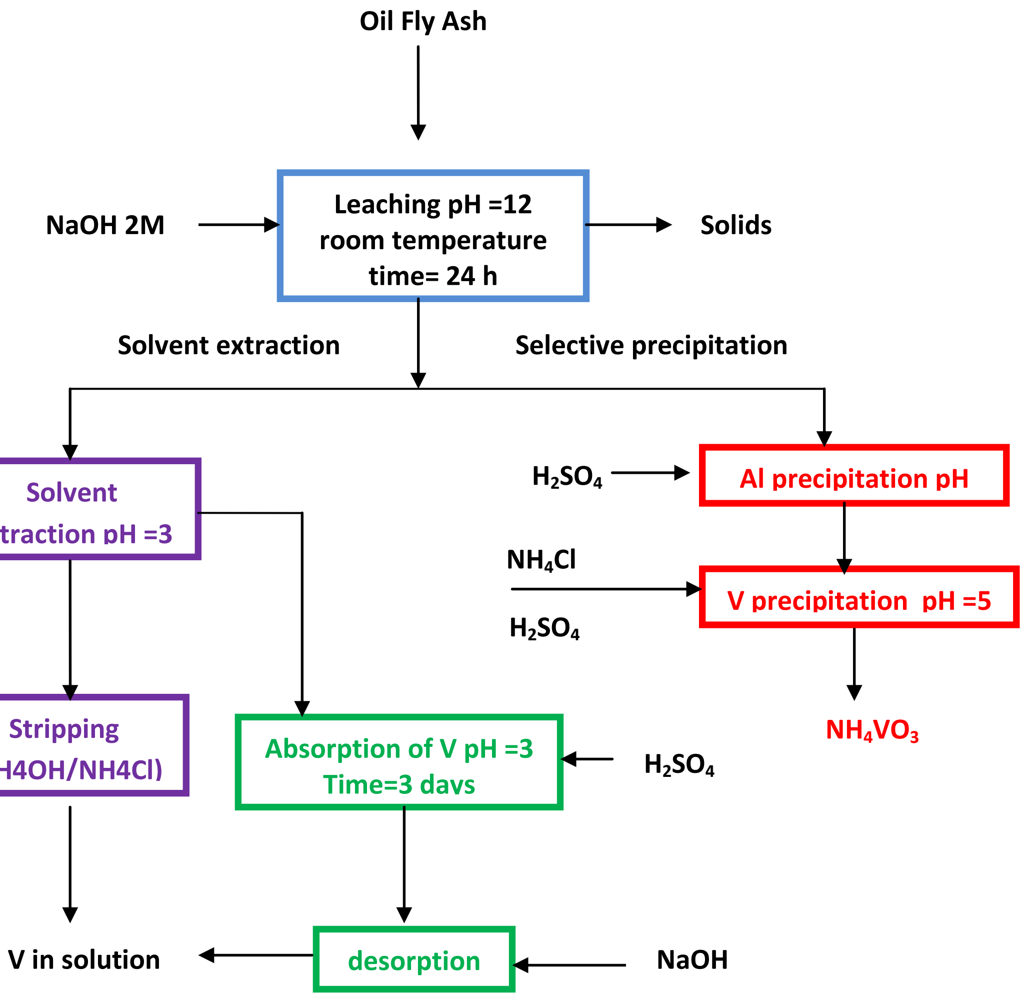


Figure 6.2 - Process of recovering oil fly ashes V (Navarro et al., 2007).

The recovery of nickel and / or vanadium from fly ashes, boiler ashes and catalysts for the production of sulfuric acid was investigated by several authors (Tsai and Tsai, 1998; Vitolo et al., 2000; Lozano and Juan, 2001, Amer, 2002; Ognyanovo et al., 2008).

2.3 Patents and industrial process

2.3.1 Gulf Process

Plant of the American company Gulf using an integrated process of hydro pyro-metallurgical melting in a furnace with an arc electric, which recovers the alumina and also metals of interest, such as Ni, Co, V and Mo. The ground ctz are subjected to calcination in the presence of soda ash (Na_2CO_3): hydrocarbons and large the sulfur is oxidized in the oven in stages, while V and Mo are converted to sodium vanadate and molybdate, water-soluble salts. The remainder of the sulfur is oxidized to sulfate and then you will have training sodium sulphate. The material is then finely ground and roasted subjected to leaching with water at about 90 ° C: the solid containing alumina, cobalt and nickel is separated by filtration and the solution containing Mo and V is subjected to removal of Al, P and As. Later, sulphate and ammonium chloride added to precipitate ammonium metavanadate at a certain pH (adjusted with H_2SO_4). The NH_4VO_3 is then calcined at 400-500 ° C to obtain pentoxide V_2O_5 having a minimum purity of 99%. Ammonia by roasting of vanadate is recovered in a series of scrubbers acids (HCl and H_2SO_4 diluted) and reused for the precipitation of vanadium.

The filtrate containing molybdenum is treated with a reducing agent, heated and acidified to obtain molybdic acid, which is recovered by precipitation. MoO_3 is obtained after calcination at 98%. Mo and V remaining in the spent solutions are recovered through solvent extraction. The solid residue of the basic leaching mainly containing Al, Ni and Co is melted in a furnace where an arc form two phases: alumina that is sold as an abrasive and refractory material and an alloy nickel-cobalt (37-43% Ni and 12-17% Co) sold to equipment capable of make the separation of the two metals (Llanos et al., 1997). The Gulf scheme of the process is shown in Figure 7.2.

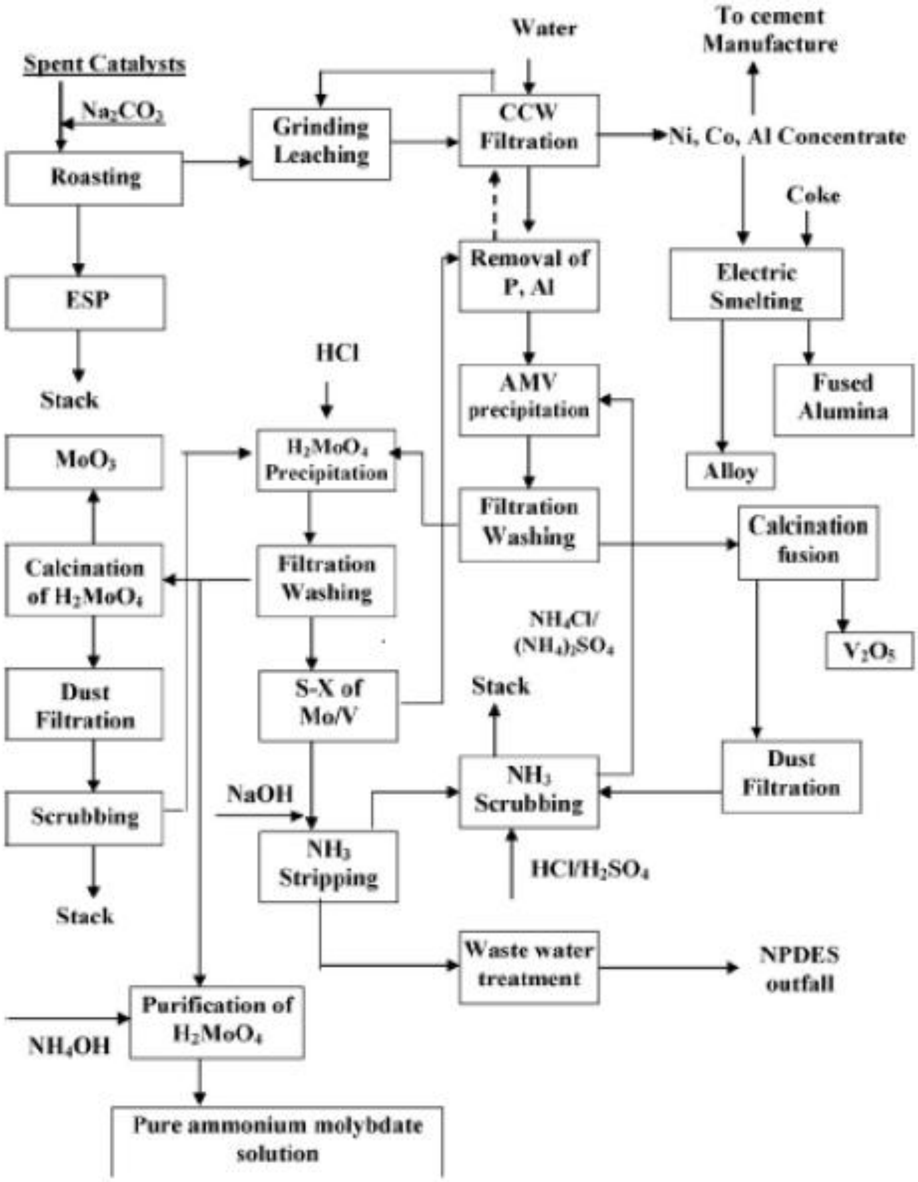


Fig 7.2 Flow sheet of Gulf process

2.3.2 CRI-MET Process

The CRI-MET system uses a basic leaching under pressure at two stages: the ctz are ground into a solution of sodium aluminate and sodium hydroxide. The resulting slurry is placed in an autoclave, where to high temperature and pressure conditions and oxidizing the sulphur is converted to sulfate, organic compounds are removed and the Mo and V converted into soluble salts.

After filtration and thickening of the suspension, the molybdenum is precipitated as MoS_3 by blowing of H_2S: molybdenum trioxide is then obtained by roasting of sulfide. The resulting solution is treated with soda to precipitate the Vanadium hydroxide, which by means of calcination is transformed into pentoxide. The solid residue of leaching is subjected to an additional caustic leaching under more oxidizing pressures, temperature and pressure, to solubilise completely alumina; what remains, essentially nickel and cobalt, is washed and calcined, and then sold to companies that operating the recovery of Ni and Co. The solution of sodium aluminate further treated to produce alumina trihydrate (Marafi and Stanislaus, 2008).

2.3.3 Eurecat Process

Eurecat initially used a combined piro-hydrometallurgic process to recover the metals. The ctz were oxidized by heat for the removal of coke, hydrocarbons and part of the sulfur and then subjected to basic leaching with soda. Mo, V, P and an small percentage of the sodium salts were converted into soluble, while the residue containing Ni, Co, Fe and Al was the most fused in arc furnace to separate the alumina from a Ni-Co alloy, while the other impurities were removed in the sludge. Ni and Co were separated by solvent extraction before of electroplating of the two metals. The solution, mainly containing molybdate and / or sodium tungstate and sodium vanadate was subjected to a purification by means of a precipitation of P and As. Resins ion exchange were used to separate Mo and V. Molybdate ammonium and vanadyl sulfate were the final products of the old process Eurecat, able to recover over 90% of Mo, V and W and about 97% Co and Ni. Currently however, the Eurocat process is completely pyrometallurgical: the ctz are fused to 1200-1500 ° C, heavy metals collect on the bottom as an alloy and are separated from the dross, consisting media inert materials, namely alumina and / or silica. This new process has the advantage of recovering 100% of the materials, as the metals are used for the production of special alloys, while the slag aggregates are sold to produce insulation materials such as rock wool (Dufresne, 2007).

2.3.4 Quanzhou Jing-Tai process

The process developed in China is quite simple and provides a leaching in the presence of hydrogen peroxide of ctz previously calcined at low temperature and ground. The leaching is led with H_2O_2 to 10-20% v / v can solubilize Mo, V, Ni and Co and leave the solid support material, ie, Al_2O_3 and SiO2, which once dried can be used in the production of bricks refractory. The leaching efficiency is approximately 95% for all four metals. The pH is then adjusted between 0.5 and 2.5 with diluted H_2SO_4, causing co-precipitation of Mo and V (99% recovery). The solution that leaving the filter increases the pH at 8.5-9.5 with sodium hydroxide: this causes the precipitation of hydroxides of Ni and Co. The solution exhausted is then subjected to ion exchange for metal recovery were dissolved, and then sent to a wastewater treatment plant before the final spill a surface water body. This process is quite simple, and operates manufacturing recovery materials close to 100% (Marafi and Stanislaus, 2008).

2.3.5 Germans processes

In Germany there are three companies that deal the recovery of metals from ctz: GfE Metalle GmbH und Materialen, AURA Metallurgie GmbH and Spent Catalyst Recycling (SCR) GmbH. The process used SCR plants plant details are not known. At GfE implantation using two processes: a pyro-metallurgical and hydrometallurgical another: the latter produces chemicals based on Mo, a solution of salts of Ni and Co and Al oxides (Fig.8.2 a). The process pyro-metallurgical instead used to treat ctz based on vanadium (sulfuric acid production, for example) and produces a concentrate of Vanadium (CVC, cast vanadium concentrates), which are derived chemicals of high purity (Fig. 8.2 b). The system of AURA is about 10000 tons / year of hydro-desulfurization catalysts ($Ni\text{-}Mo/Al_2O_3$ and $Co\text{-}Mo/Al_2O_3$). It produces a hydrated oxide of Mo; Mo concentrates, ammonium molybdate, sulfate of Ni and Co mixed plaster and aluminum oxide (Marafi and Stanislaus, 2008). Cobalt and nickel are precipitated as hydroxides by adding NaOH and bringing the pH to 12. Aluminum is precipitated at pH 7-8 instead with the addition of sulfuric acid. The molybdenum is recovered through solvent extraction (MIBK) and subsequent crystallization of epta-molybdate ammonium $(NH_4)_7Mo_6O_{24} \cdot 4H_2O$.

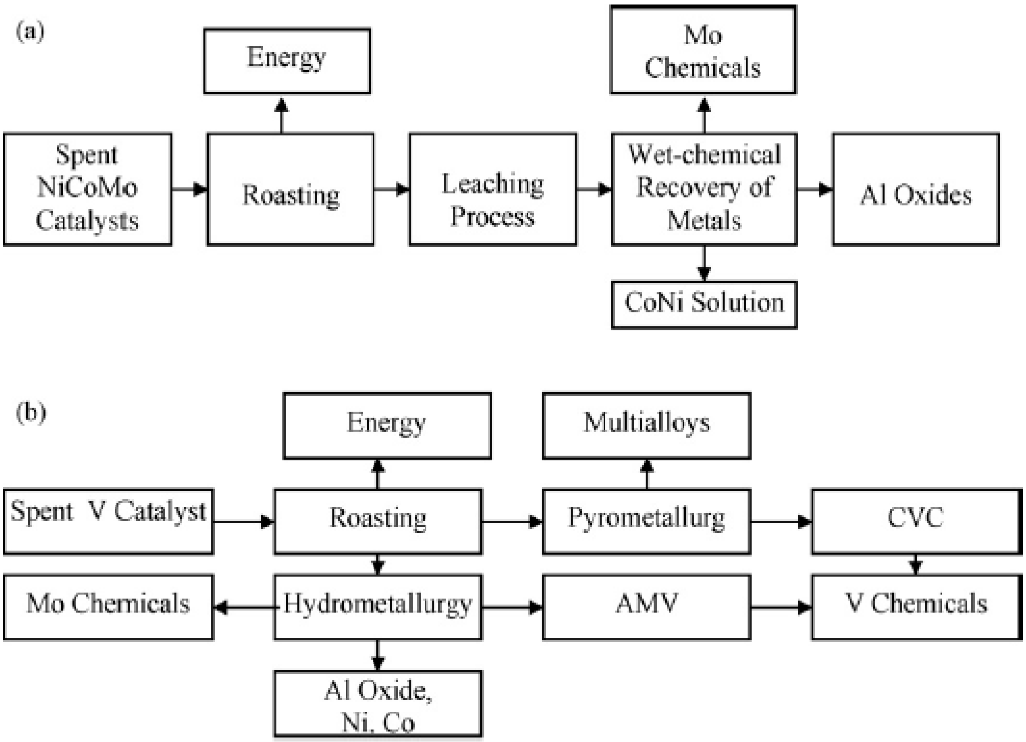


Figure 8.2 - Process GfE: hydrometallurgical (a) and pyrometallurgical (b).

2.3.6 Other patented processes

The patented process by sedem (Belgium) provides for the chlorination of hydro-desulfurization ctz (previously purified from possible hydrocarbon) at temperatures of 200-400 ° C using Cl_2, steam Water and HCl gas. Form volatile chlorides and oxides ($AlCl_3$, MoO_2Cl_2 and $VOCl_3$) that are adsorbed from a solution in a scrubber saturated with HCl at 60 ° C. Cobalt and nickel remain in solution as $CoCl_2$ and $NiCl_2$. Aluminum is recovered from the solution that collects in the bottom of the column by precipitation in the form of chloride hexa-hydrate. The two solutions containing chlorides of Mo and Ni-Co-V must be subjected to the selective recovery of metals, operations not specified in the patent (Commander et al., 1981). Amax Inc., USA, patented an integrated process for the recovery of all metals as catalysts exhausted in 1985. The process based on oxidation in the presence of Na_2CO_3 in water and O_2 can solubilize and neutralize Mo and V simultaneously Sox (Formation of Na_2SO_4). Oxidation occurs at about 300 ° C and 130 atm. The solid is again placed in an autoclave for further digestion caustic (NaOH 10%) to 250 ° C with the purpose to dissolve the alumina (~ 95%). After filtration, the residue contains about 7% Co, 8% Ni and 5% of Al in the form of oxides CoO, NiO and Al_2O_3. The solution containing Mo and V is acidified with H_2SO_4 to pH <1 (conc. 3N) at 80 ° C it adds that causes the precipitation of H_2S MoS_3, while the vanadium remains in solution as $VOSO_4$ (vanadyl sulfate). Once filtered is add NaClO3 in a way that the ion VO^{2+} is oxidize to VO^{3+} at room temperature, then NaOH to pH 2.5. The solution is brought to a boil for 30 minutes and, once cooled, is observed the precipitation of a salt orange ($Na_2H_2V_6O_{17}$). Salt is again dissolved and the vanadium is precipitated as NH_4VO_3 by adding of H_2SO_4 and $(NH_4)_2SO_4$ in appropriate conditions. The vanadate was then converted to V_2O_5 prior roasting (Sebenick et al., 1985). Hyatt has proposed a process that involves a leaching autoclave ctz of Ni and Co-Mo-Mo in sulphuric acid solution in an atmosphere of H_2S 10 atm and a temperature of 150 ° C for 1 h. In the reactor are added 2 kg of 98% H_2SO_4 and 7-8 liters of water per kg of ctz. Aluminium support is solubilized in the form of $Al_2(SO_4)_3$, while Mo, Ni and / or Co precipitate as sulfides. The precipitate is separated from the solution aluminium sulfate by filtration, and can be sold as concentrated as it is, alternatively, the concentration of sulfides is re-oxidized in aqueous solution in an autoclave at 200 ° C with oxygen at 15 atm for 2 h. The molybdenum is oxidized to $MoO_3 \bullet H_2O$ (acid molybdic), while NiS and CoS are translated to their sulphates. The suspension is cooled to room temperature and molybdic acid can be recovered by filtration. The filtrate can be subjected electrolysis, ion exchange (Amberlite resins) or extraction solvent to recover Ni and Co (Hyatt, 1987). Chevron Texaco Corporation (USA) has patented in 2007 new process for the recovery of Mo, Ni and V from spent similar to Lc-ctz Finer. This is ctz hydrocracking and then having a relatively percentage of residual liquid hydrocarbons: they are removed by cleaning solvent (xylene, toluene or kerosene) is then naturally regenerated by distillation. The CTZ is then subjected to a leaching in aqueous solution at 90-200 ° C in an autoclave where it is placed ammonia to 20-50 atm. This will form $(NH_4)_2SO_4$ and NH_4VO_3 and $Ni(NH_3)_6SO_4$. The ammonium metavanadate precipitate and is removed by filtration, and then be re-dissolved in an ammonia solution from which it crystallized in almost pure form. By V_2O_5 can get it at the appropriate temperature for roasting. The solution containing Ni and Mo is subjected to a solvent extraction (kerosene) in which the Ni is extracted in the organic phase (LIX-84-I) at pH 8.5 and then stripped with H_2SO_4. Later in the aqueous stage is added $MgSO_4$ to remove arsenic and phosphorus. Finally the pH is brought to 3-4 with sulphuric acid and ammonium molybdate may be crystallized in an almost pure. The stock solution resulting from the filtration of the crystallized is subjected to solvent extraction for the recovery of the remainder of Mo (Marcantonio, 2007). Toyabe et al. have patented a process for the recovery of Al, Ni, Mo, V and Co from spent hydro-processing catalysts. This process provides an initial roasting between 400 and 1000 ° C for the removal of coke and sulphur, then roasted ctz are subjected to a dissolution by sulphuric acid in the presence of aluminum as a catalyst dissolution. The aluminum is precipitated as ammonium aluminum sulfate, possibly after removing the iron is present in the CTZ. Mo and V are recovered by two extractions with different solvents. The pH solution is then increased for precipitation of Ni and Co in the form of hydroxides.

CHAPTER THREE

AIM OF WORK

The objective of this work was the treatment of spent refinery catalysts by the sulfide precipitation to reduce their environmental hazard; at the same time try to recover the metals present into the spent catalysts by selective precipitation in order to obtain four “concentrated products” each of which rich in molybdenum, nickel, vanadium and aluminium respectively. The sulfide precipitation occurred by stoichiometrically adding of Na_2S and by the biological production of H_2S gas mediated by sulfate- reducing bacteria for the treatment of these dangerous and toxic solid wastes permit the development of an environmental friendly process.

The H_2S gas was produced biologically by sulphate-reducing bacteria in an Anaerobic Baffled Reactor (ABR) fed continuously; the H_2S gas produced was then sent in a separated chemical reactor containing the synthetic leaching or bioleaching solution where the reactions of precipitation occurred.

Based on the previous research, preliminary studies and the hypotheses described above, the following aims were formulated for the present work:

- Evaluate the possibility to treat these spent catalysts by direct contact between SRB and base metals solution;
- Evaluate the possibility to treat these spent catalysts by indirect mechanism where the SRB and base metals solution were in two separated reactor;
- Determine the possibility to remove selectively the heavy metals as sulfide compounds and also hydroxide/oxide compounds;
- Asses the possibility to treat these spent refinery catalysts by H_2S gas biologically produced and not only by stoichiometrically adding of Na_2S compound;
- Determine if is possible to treat the spent refinery catalysts by biological H_2S gas using synthetic metals-containing solutions with the same concentrations of base metals of a solution derived from acid leaching process;
- Asses the purity degrees of concentrated obtained after the precipitation;
- Experimental data were used to do a preliminary technical-economical evaluation by apposite software.

CHAPTER FOUR

MATERIALS AND METHODS

In this chapter are reported the principal experimental methods used together a brief description of the same. About the simulation process was used the commercial software *SUPER PRO DESIGNER V5.1*. In the first part of the chapter are shown the experimental and analytical methods used for the development of process to selective precipitation of base metals containing into spent refinery catalysts by adding of Na_2S compounds, ”chemical process”.

In the second part are shown the experimental and analytical methods used for the development of process to selective precipitation of molybdenum, nickel, aluminum and vanadium from synthetic base metals solution with H_2S gas, produced by sulfate reducing bacteria in an lactate fed anaerobic baffled reactor, “biological process”.

4.1 Materials and methods “chemical process”

4.1.1 Synthetic base metal solutions

Synthetic leach and bioleach liquors were prepared with analytical grade $NiSO_4$, $VOSO_4$, MoO_3 and Al_2SO_4 (Merck and Sigma Aldrich). Solutions resembling leach liquors obtained by chemical leaching and bioleaching were formulated as detailed in Table 1 according to literature data (Ferella et al., 2011; Beolchini et al., 2009).

	Al (M)	Mo (M)	Ni (M)	V (M)
synthetic bioleach liquor	0.0032	0.0022	0.0063	0.016
synthetic leach liquor	0.055	0.16	0.085	0.15

Table 1.4 Synthetic leach liquors resembling metal solution obtained after bioleaching and after chemical leaching.

4.1.2 Preliminary tests of metal precipitation at different pH

Precipitation tests were performed with single metal solutions utilizing the typical concentration of bioleach liquor for all four metals investigated and multi metal solutions (bioleach liquor and leach liquor). Each metal system was brought to the desired pH (0, 0.5, 1, 3, 6 and 9 units) by using H_2SO_4 and/or NaOH and measuring pH by a glass pH electrode (Crison GPL 22). Metal precipitation was performed with and without adding Na_2S (0.03M and 0.3M for bioleaching and leaching, respectively. After 1h stirring suspension samples were collected, filtered and liquid phase was analyzed by an Inductively Coupled Plasma Emission Optical Spectrophotometer Varian Vista MPX (CCD simultaneous ICP-OES).

4.1.3 Sequential precipitation of metals

Sequential precipitation of metals was performed according to two schemes (A and B) reported in tables 2.4 and 3.4. In the first scheme Al was removed after Ni, while in the second scheme Al was precipitated as first metal. Al precipitation was obtained by adding of Na_2S (0.03-0.3M).

According to these precipitation schemes, to 1L of bioleach liquor and leach liquor were added the precipitating chemicals for the first precipitation step (i.e. NaOH up to pH 4 according to the B scheme). After 1h stirring, suspensions were filtered for solid/liquid separation. An aliquot of liquid was analyzed by ICP-EOS, and a sample of dried solid was dissolved in aqua regia (hydroclhoric acid and nitric acid (ratio 3:1 v/v) diluted and analyzed by ICP-EOS Vista MPX (CCD simultaneous ICP-OES).

Liquid phase was then used for the second precipitation step (i.e. H_2SO_4 solution and Na_2S were added to have pH 0.5 in the second step of B scheme). After each step analyses of solid and liquid samples were performed as described before.

	Precipitation Scheme A			% Metal precipitation							
Precipitation step	Operating conditions		Target Metal	Leach liquor				Bioleach liquor			
	pH	Na_2S		Mo	Ni	Al	V	Mo	Ni	Al	V
I	0.5	Yes	Mo	20	10	15	3	79	13	9	2
II	3.5	Yes	Ni	55	36	23	19	15	41	12	11
III	4	No	Al	13	11	61	65	0	2	58	62
IV	6	No	V	6	7	0	11	1	7	20	22

Table 2.4 Operating conditions and metal precipitation for sequential precipitation scheme A.

	Precipitation Scheme B			% Metal precipitation							
Precipitation step	Operating conditions		Target Metal	Leach liquor				Bioleach liquor			
	pH	Na_2S		Mo	Ni	Al	V	Mo	Ni	Al	V
Zero	4	No	Al	4	19	55	7	5	9	65	12
I	0.5	Yes	Mo	75	3	4	6	87	38	0	5
II	3.5	Yes	Ni	12	54	26	19	7	52	8	17
III	6	No	V	6	21	8	67	1	0	26	64

Table 3.4 Operating conditions and metal precipitation for sequential precipitation scheme B.

4.2 Materials and methods “biological process”

4.2.1 Preliminary test of precipitation by direct mechanism

The direct mechanism of precipitation was conducted by the direct contact between the synthetic base metals solution (bioleach liquor) and the sulfate reducing bacteria: the synthetic metals solution was added inside the SRB growing batch (total volume 100 ml) and after 15 days the precipitates formed were removed by solid/liquid separation; the solids obtained were dissolved in strong acid ambient and then analyzed by ICP-OES instrument.

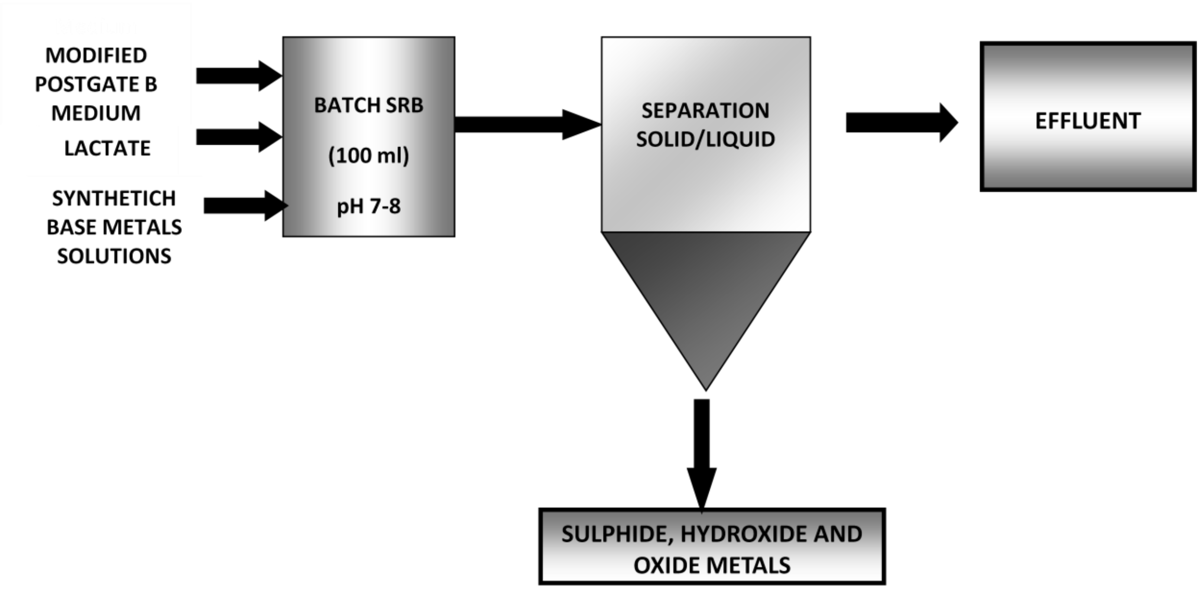


Figure 1.4. Schematic diagram of the direct process.

4.2.2 Preliminary test of metals precipitation by indirect mechanism

The preliminary indirect mechanism in figure 2.4 showed was performed by using of two flasks (250 ml), where in one were growing the SRB and the H_2S gas produced was carried by peristaltic pump in the second flask contained the synthetic bioleach liquor.

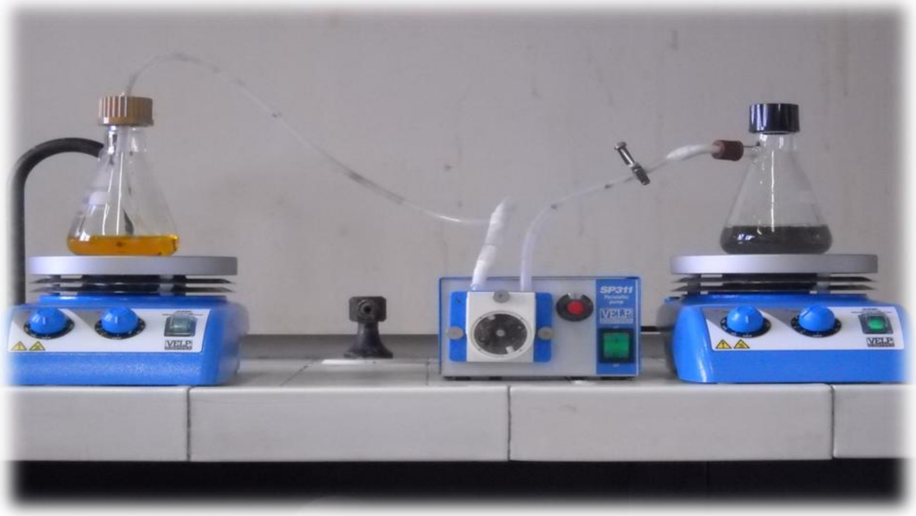


Figure 2.4. Laboratory scale system of preliminary indirect precipitation test

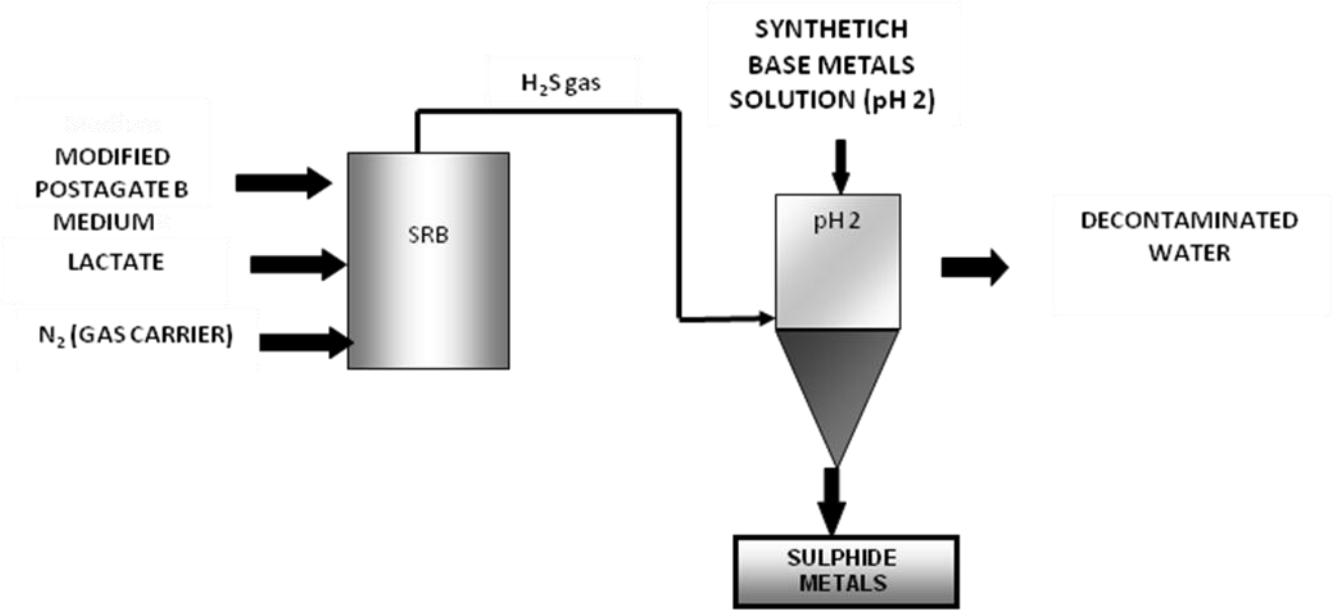


Figure 3.4. Schematic indirect mechanism diagram of base metals precipitation.

4.2.3 Bioreactor set-up

The sulfate reducing anaerobic baffled reactor (ABR) had four chambers and a total liquid volume of 28 L (PFWA, plastic fabrications WA) (Figure 4.4). The ABR was inoculated with a mixture of sulfate reducing bacteria cultures enriched from samples obtained from Alcoa residue area, Western Australia, and anaerobic sludge obtained from Woodman Point wastewater treatment plant in Western Australia. The bioreactor was fed with modified Postgate B medium (Table 1) and sodium lactate as electron donor.

Figure 4.4. Photography of anaerobic baffled reactor during the experiment; on the right side is showed also the separated column precipitation reactor.

Lactate was added (1.23 g/L) stoichiometrically to sulfate according to the following Reaction:

$$2CH_3CHOHCOOH + 3SO_4^{2-} \rightarrow 3H_2S + 6HCO_3^{-}$$

The influent solution was divided into two containers: one of which contained sodium lactate solution and the other the modified Postgate B medium as reported in Table 4. The reactor was operated in continuous flow mode to produce H_2S with a hydraulic retention time (HRT) of 5 days for 70 days at room temperature.

Compound	**Concentration (g/L)**
NH_4Cl	1
Na_2SO_4	4.5
$CaCl_2 \cdot 6H_2O$	0.06
$MgSO_4 \cdot 7H_2O$	0.06
Yeast extract	0.1
KH_2PO_4	0.5
Ascorbic acid	0.05
Na-thioglycollate	0.05
$FeSO_4 \cdot 7H_2O$	0.1

Table 4.4 Composition of sulfate reducing bacteria growth medium (modified Postgate B medium, pH 5.2 prepared in tap water.

The following schematic diagram of process with ABR (figure 5.4) shown the different steps of base metals precipitation; the aluminum precipitation step is not showed because it was precipitated before all of other metals at pH 4. The N_2 gas carrier permitted the escaping of H_2S gas contained into the bioreactor.

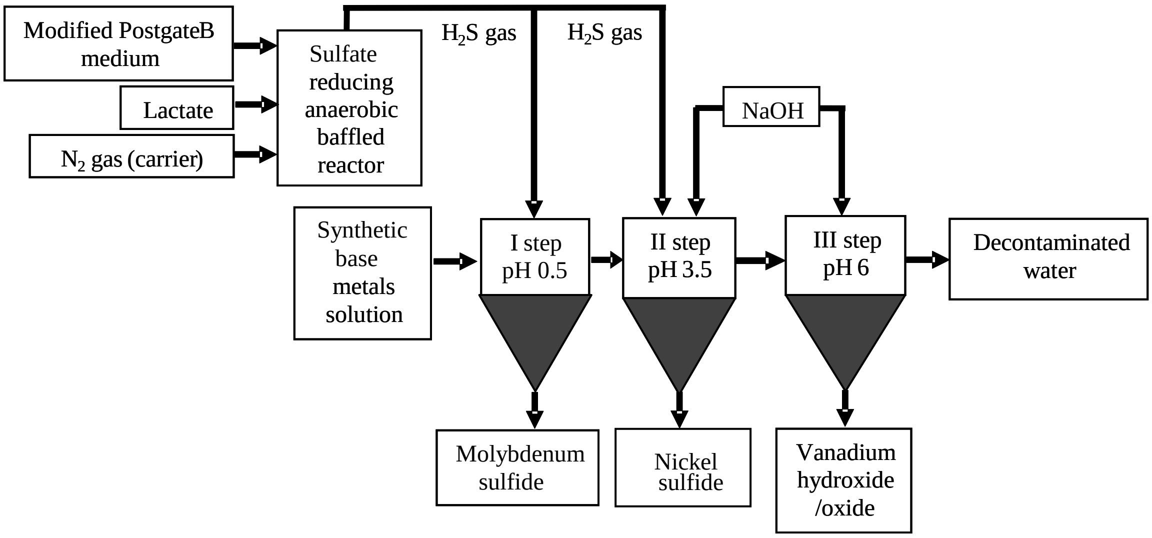


Figure 5.4. Schematic diagram of the process with ABR and separated units for the selective precipitation of heavy metals investigated.

The samples were taken 3 times per week from bioreactor influent and effluent to measure the sulfate concentration, total organic carbon, total alkalinity, pH, ORP and dissolved sulfide concentration.

4.2.4 Precipitation of metals with biogenic H_2S

The H_2S gas produced by SRB in the ABR was stripped with N_2 gas carrier into a cylindrical glass reactor (total height 50 cm, inner diameter 4 cm) where the H_2S was allowed to react with a heavy metals solution, which contained Mo, Ni and V. In according with chemical equilibrium diagram Medusa software the selective precipitations were made at different pH values to obtain aluminum hydroxide ($Al(OH)_3$) at pH 4, molybdenum sulfide (MoS, MoS_2) at pH around 0.5, nickel sulfide (NiS,) at pH value 3.5 and vanadium oxide at pH value 6. Vanadium and aluminum were precipitated by adding of NaOH. Three different synthetic heavy metals solution were used (Table 5) to assess the effect of increasing heavy metals concentration on the precipitation efficiency (%) and the purity of the precipitates. The synthetic base metal solutions were prepared in distilled water with analytical grade MoO_3, $NiSO_4$, $VOSO_4$ (Merck and Sigma Aldrich chemicals). The synthetic base metals solutions investigated were prepared to simulate the solutions obtained from leaching and bioleaching processes of spent refinery catalysts (table 5.4); the solution 1 and 2 were prepared in according with leaching experiments conducted by Ferella et al (2011) and bioleaching experiments conducted by Beolchini et al (2009), respectively while the solution 3 had a very low heavy metals concentration. All precipitation experiments were conducted at room temperature.

	Mo	Ni	V
Solution 1 (leach liquor)	0.16	0.085	0.15
Solution 2 (bioleach liquor)	0.022	0.006	0.016
Solution 3 (bioleach liquor (-))	0.0004	0.001	0.0019

Table 5.4. Heavy metals concentrations (M) in the synthetic heavy metal solutions used for precipitation experiments.

4.2.5 Analytical methods

Solution pH was measured in unfiltered samples using a glass pH electrode (pH 330i merck PTY, SEN TIX H 3mol/KCl) and redox potential by SEN TIX ORP electrode (3mol/KCl). Sulfate concentrations were determined by ion chromatography (Dionex ICS-3000). The samples for sulfate analysis were centrifuged to remove particulate matter, and supplemented with lithium fluoride as internal standard. Total dissolved sulfide was analyzed using filtered samples spectrometrically using a UV Unica helios epsilon following the method described by Cord-Ruwisch (1985). Samples for metal determinations were filtered through 0.45 µm filters (Millipore), and then acidified with concentrated HCl to pH around 1.0 and finally analyzed with an Atomic Absorption Spectrometer (AAS varian spectra). The dissolved total organic carbon was measured with a TOC, TOC-VCSH total organic carbon analyzer (Shimadzu). Total alkalinity was analyzed by tritating unfiltered samples with 0.1 M HCl to pH 4.5 according to the standard SFS-EN ISO 9963-1. The scanning electron microscopy (SEM) analysis of the metal precipitates was conducted with SEM LEO1450VP and energy dispersive X-ray spectrometry (EDS) with EDS INCA300 and INCA software by chemistry department of Rome university "La Sapienza". The precipitate sample has been grounded by to reduce the size of precipitates granules.

4.2.6 Preliminary studies of chemical speciation of the base metals by MEDUSA software

MEDUSA: Make Equilibrium Diagrams Using Sophisticated Algorithms, is a program that permit to obtain a preliminary chemical speciation of the elements varying different factors as pH, ORP, ionic strength, elements concentrations, temperature considering at the same time the interaction between the different elements selected.

By Medusa it was possible to get information about the form (liquid or/and solid) of base metals investigated (molybdenum, nickel, vanadium and aluminum) varying the pH and the metals concentration.

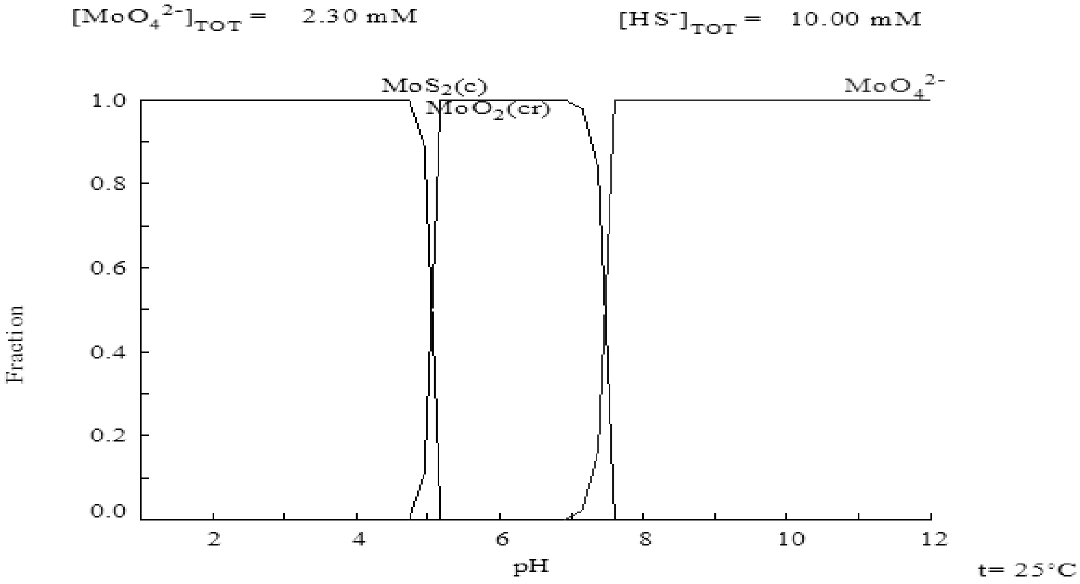


Figure 6.4. Chemical speciation of molybdenum in presence of sulfide varying the pH values, by *MEDUSA* software.

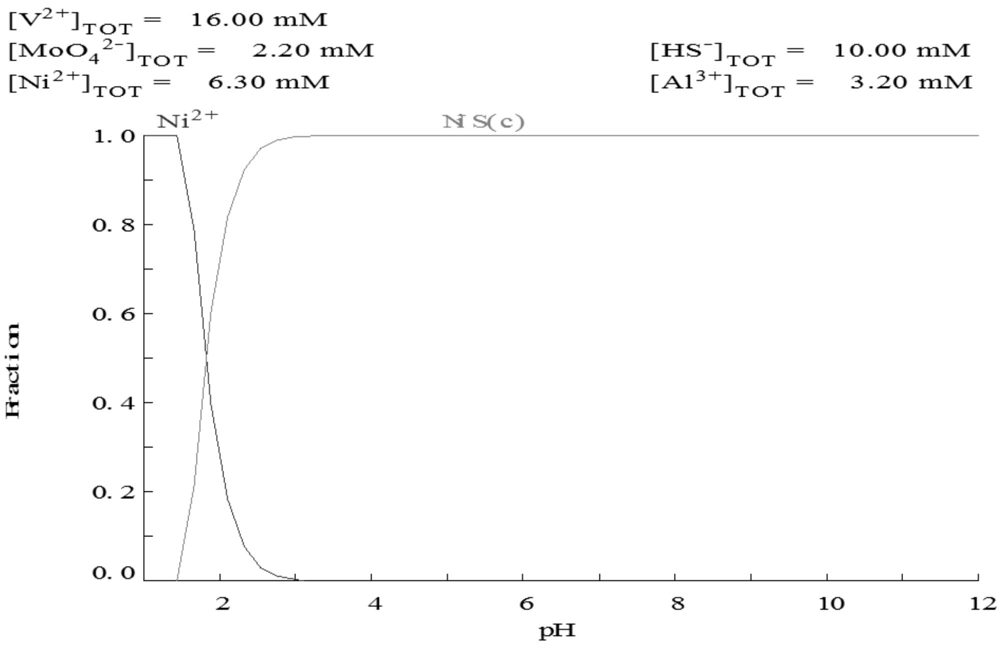


Figure 7.4 Chemical speciation of nickel in presence of sulfide varying the pH values, by MEDUSA software.

4.2.7 Technical and economical preliminary simulation of process by Super Pro Designer software

Super pro designer software is a computing program for designing and optimizing integrated specialty chemical, biochemical, pharmaceutical, consumer product, food, agricultural, hydrometallurgical, packaging, as well as water purification, wastewater treatment and air pollution control processes. In figure 8 is showed an example of Super Pro designer flow sheet.

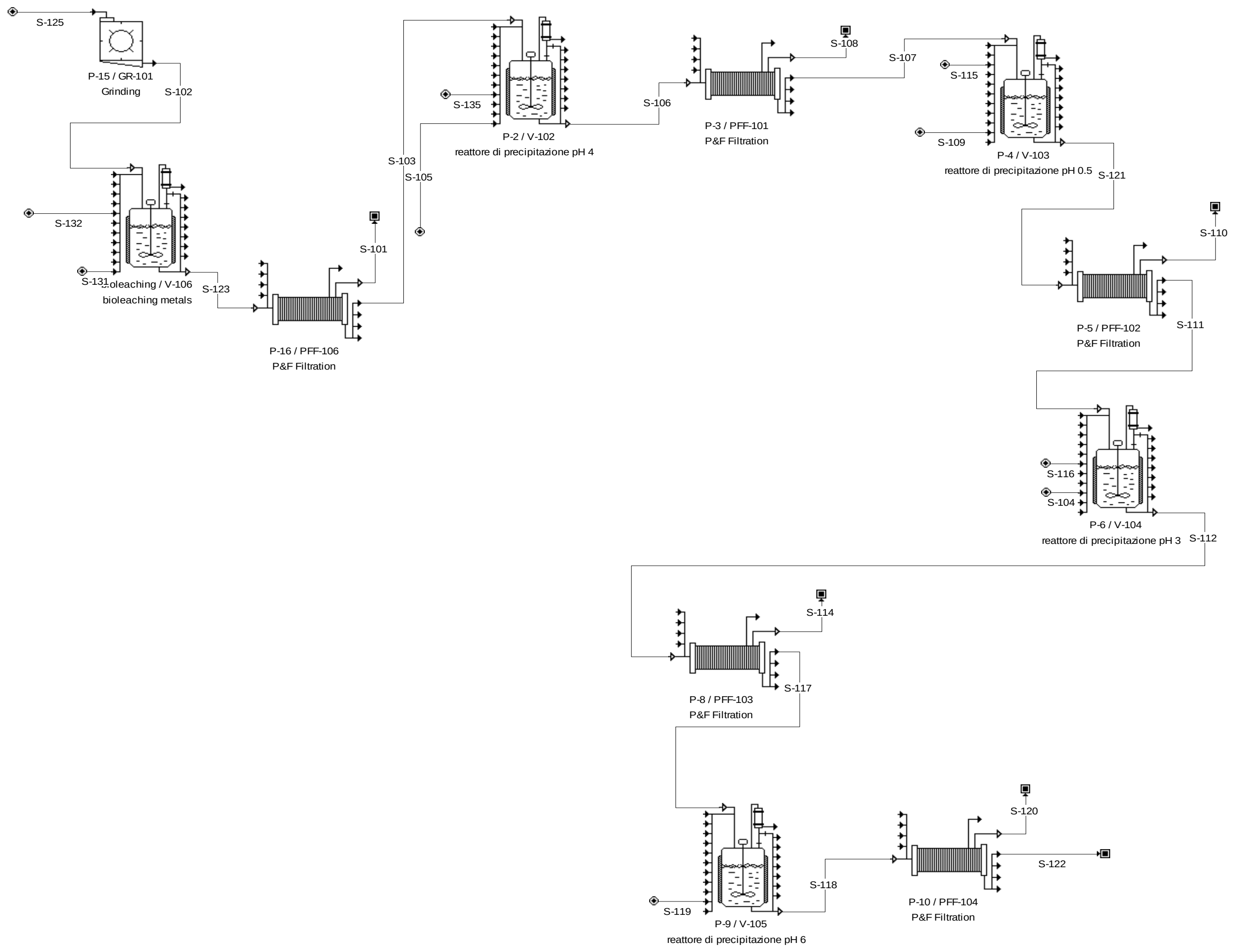


Figure 8.4 Super Pro simulation flow sheet of selective recovery of base metals by adding of Na_2S.

CHAPTER FIVE

RESULTS

5.1 Precipitation of base metals by direct mechanism

5.1.1Effects of base metals on bacterial growing

The precipitation tests by direct mechanism have been conducted in batch (100 ml) where the synthetic base metals solution was in direct contact with sulfate reducing bacteria; the experiments were conducted at room temperature for 15 days and after the precipitated obtained were analyzed by ICP-OES. During the experiments several factors has been monitored as the base metals concentration, pH, ORP and the removal of sulfate.

$$2\,CH_2O + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^-$$

$$H_2S + M^{2+} \rightarrow MS(s) + 2H^+$$

As showed in reaction 1 and 2, the sulfate reducing bacteria by their metabolic activity to reduce the sulfate to sulfide; therefore the reduction of sulfate concentration in the batch means that the bacteria activity is going on.

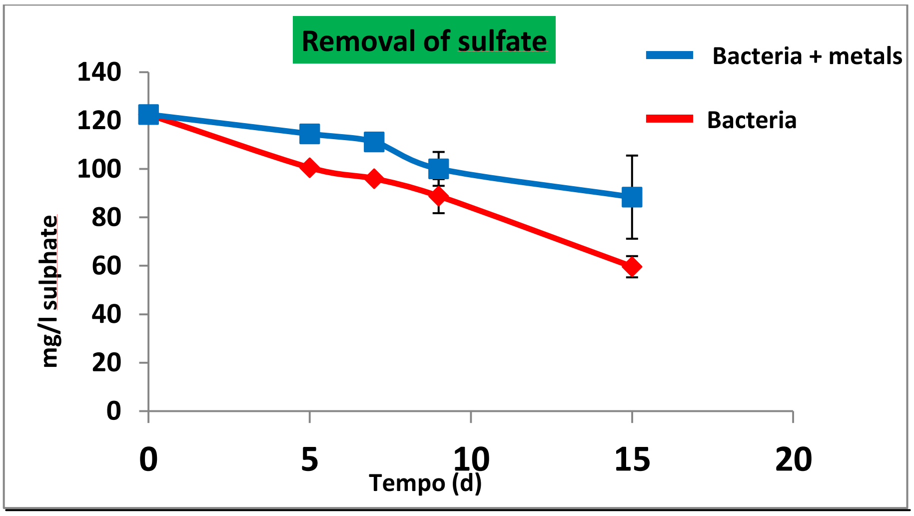


Figure 1.5 Removal of sulfate in presence and absence of base metals in the growing bacteria batch.

As showed in figure 1.5, the presence of base metals was cause of adversely effects on the capacity of the sulfate reducing bacteria to reduce the sulfate concentration and consequently on the production of H_2S gas. The direct contact between synthetic base metals solution and SRB has adversely effects also on the pH and ORP of postgate B medium growing of bacteria.

About the pH and ORP profile (figure 2.5 and 3.5), the presence of synthetic metals solution was cause of decreasing of pH value and increasing of ORP (oxidation reduction potential) value.

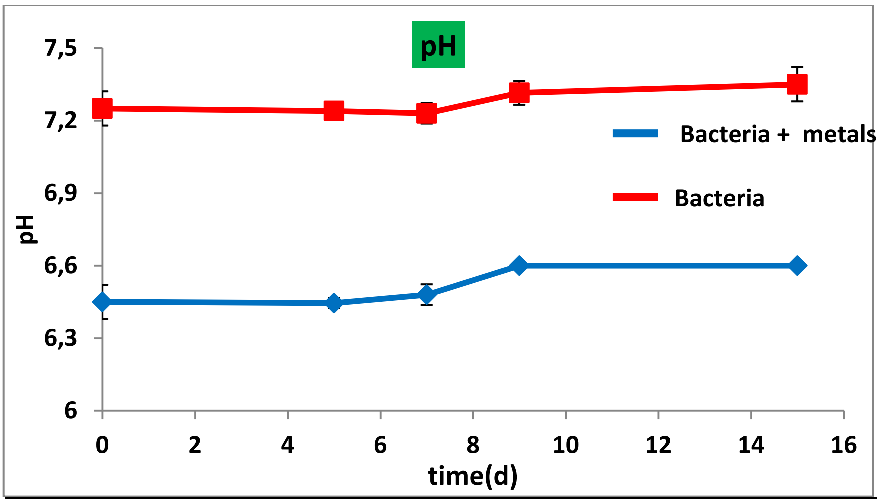


Figure 2.5 The varying of pH values in presence of base metals.

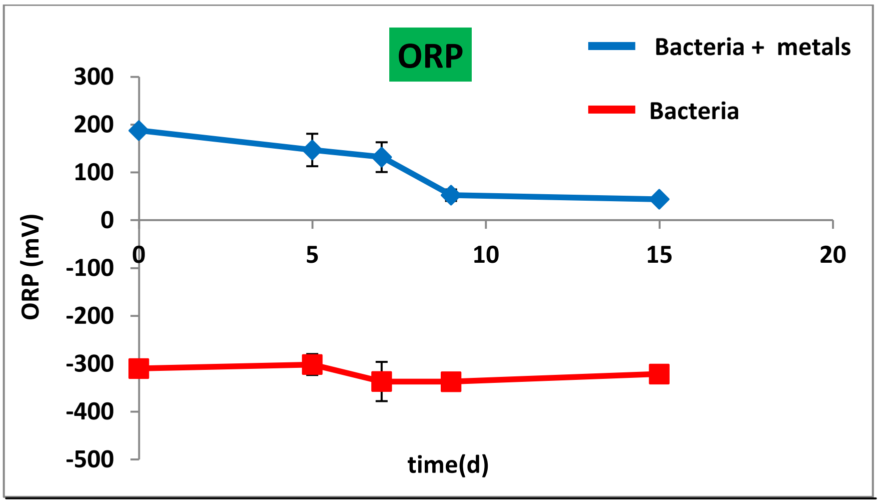


Figure 3.5 The varying of ORP values in presence of base metals.

The results of ICP-OES analysis conducted on precipitates obtained (after digestion with aqua regia) are reported in the figure 4.5.

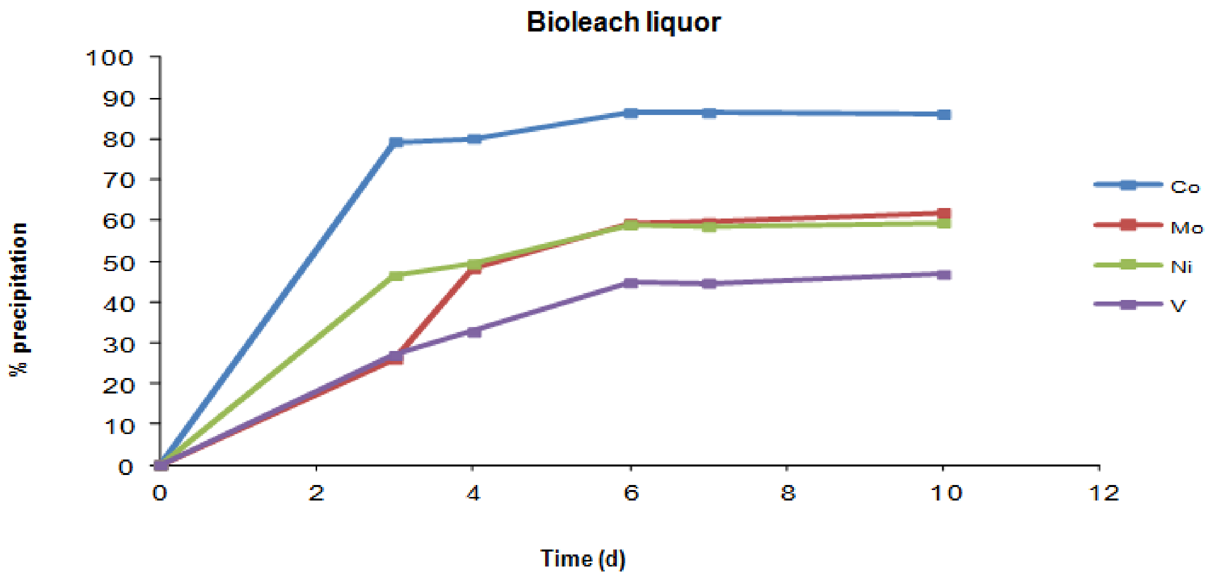


Figure 4.5 Precipitation of base metals (cobalt, molybdenum, nickel and vanadium) occurred with synthetic bioleach liquor by direct precipitation.

The precipitation of metals by direct mechanism occurred totally by 6 days; the percentages of precipitation were very similar (50%) for vanadium, nickel and molybdenum while cobalt precipitation reached 80%. The precipitations were simultaneous due to the pH value of growing medium that was around 7; at these pH values the precipitation of metals in solution occurred not only as sulfide compounds due to the HS^- produced by bacteria but also as hydroxide/oxide compounds.

5.1.2 Preliminary experiments of indirect mechanism of metals precipitation by lab scale system

The indirect precipitation was conducted utilizing the H_2S gas produced by SRB to precipitate the base metals containing in synthetic leaching and bioleaching solutions in an separated reactor (see chapter four); as illustrated in figure 5.5, the H_2S gas was carried out by N_2 (gas carrier) and with help of peristaltic pump was convoyed in a precipitation reactor with the pH value settled to 2.

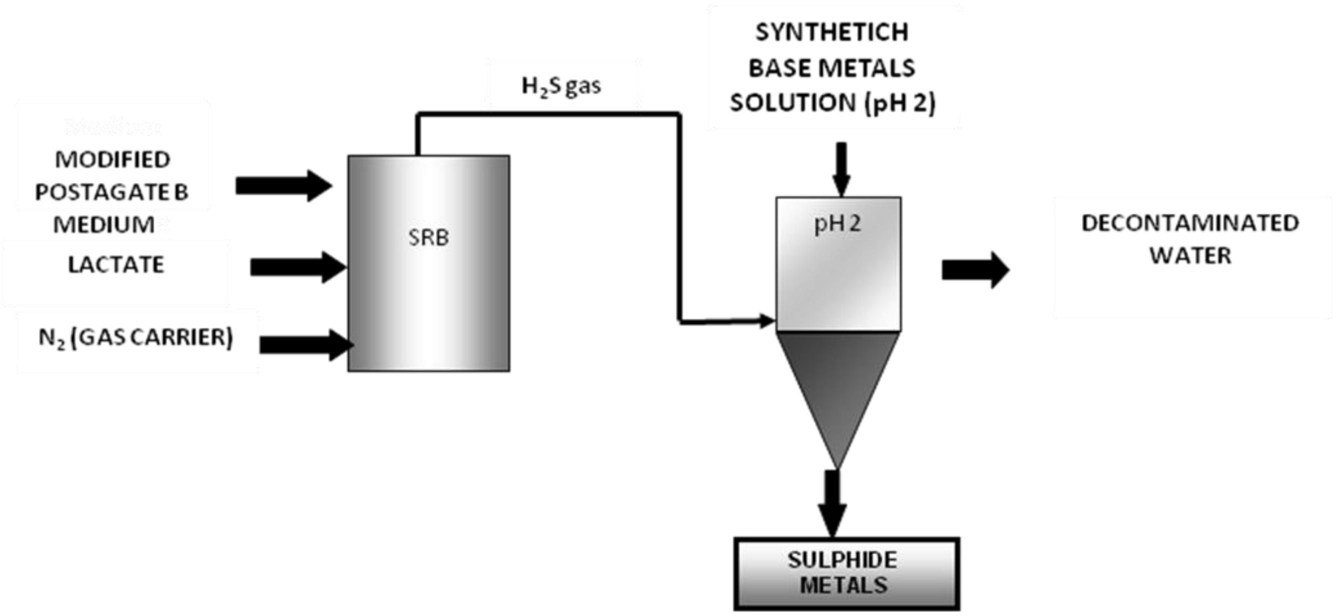


Figure 5.5 Scheme of indirect precipitation.

The purity indices of precipitates obtained has been calculated in according with the following equation:

Precipitate pure degree= mg*(prec.)/mg tot

Where
mg*(prec)= mg of single metal target precipitated at pH value 2;
mg tot= total mg precipitated of all four metals at pH value 2;

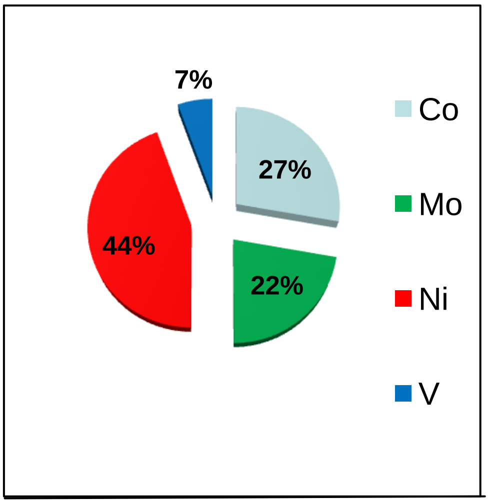


Figure 6.5 Black sulfide metals.

Figure 7.5 Purity indices of precipitates at pH 2.

As shown in figures 6.5 and 7.5 the precipitation occurred by indirect mechanism: in figure 6.5 are showed the black sulfide compounds on the bottom of the flask due to the reaction between the H_2S gas biologically produced and the metals dissolved in synthetic solution. In figure 7.5 are reported the w/w (mg met/mg met tot) of precipitates obtained.

5.1.3 Preliminary chemical speciation studies by Medusa software

Based on the results obtained with direct and indirect precipitation, where the selective precipitation did not occur, chemical speciation studies has been done for all four metals investigated in order to find the path of selective recovery of them.

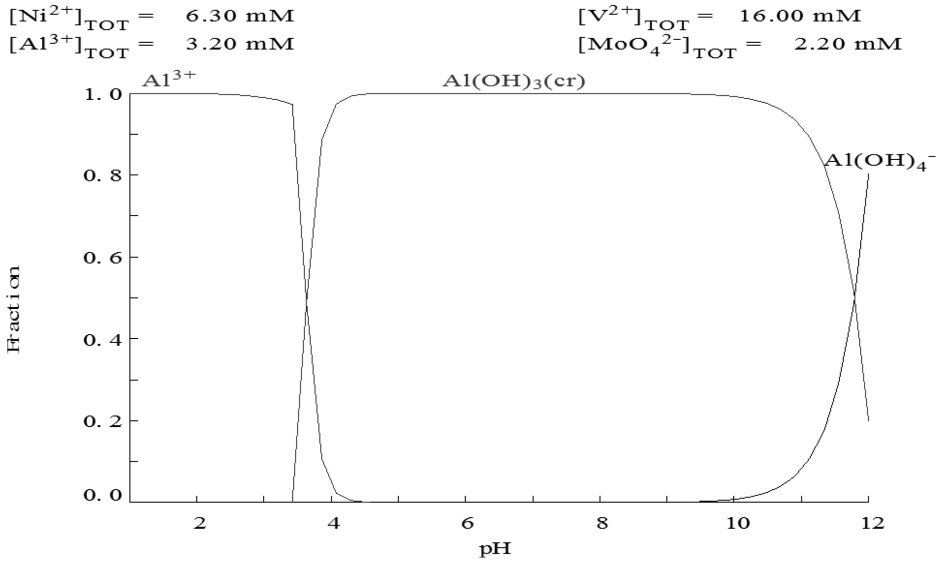


Figure 8.5 Chemical speciation diagram of aluminum (bioleach liquor).

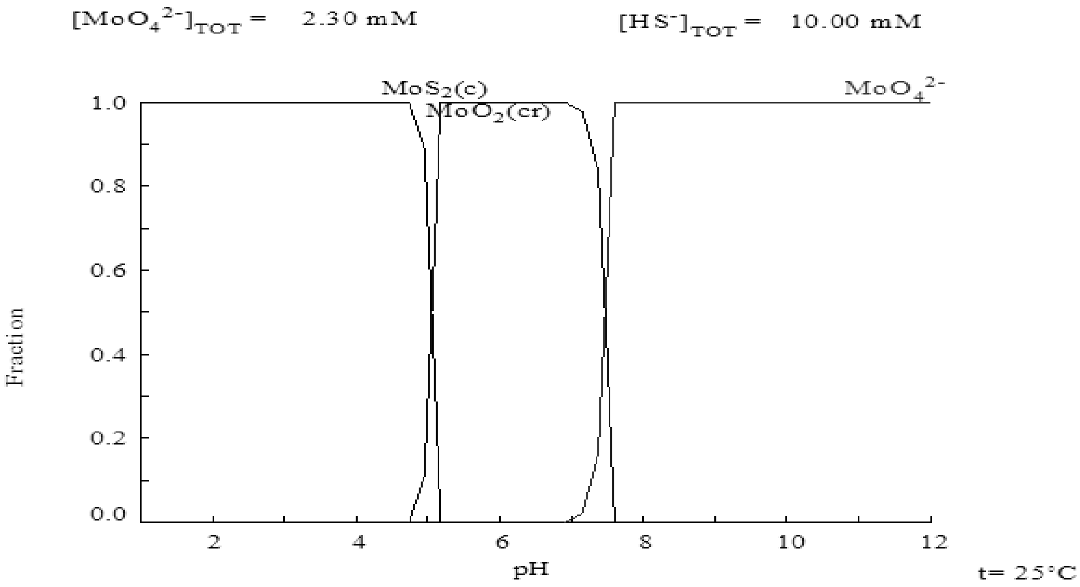


Figure 9.5 Chemical speciation diagram of molybdenum (bioleach liquor).

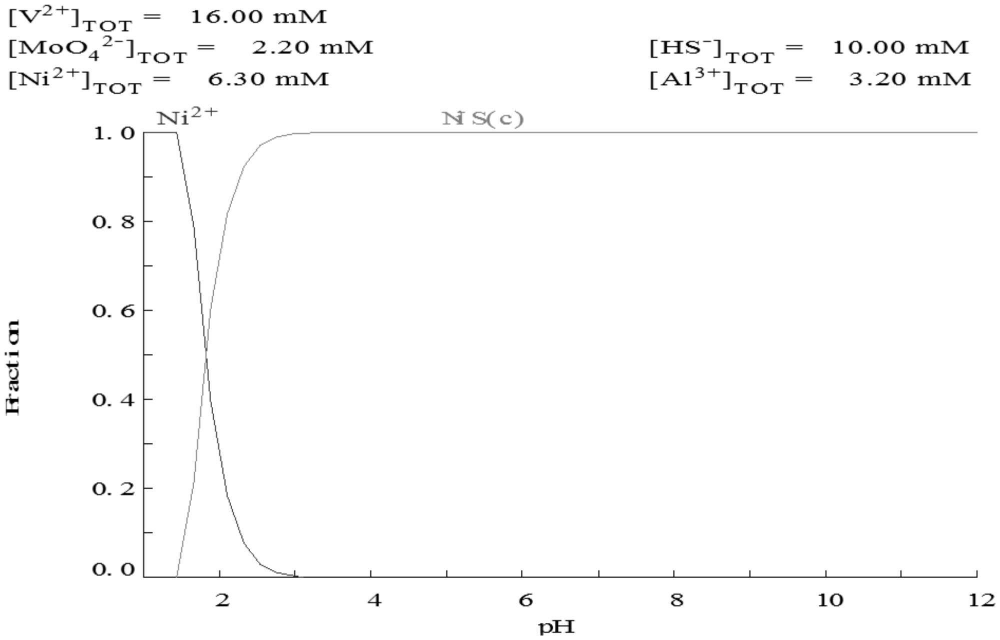


Figure 10.5 Chemical speciation diagram of nickel (bioleach liquor).

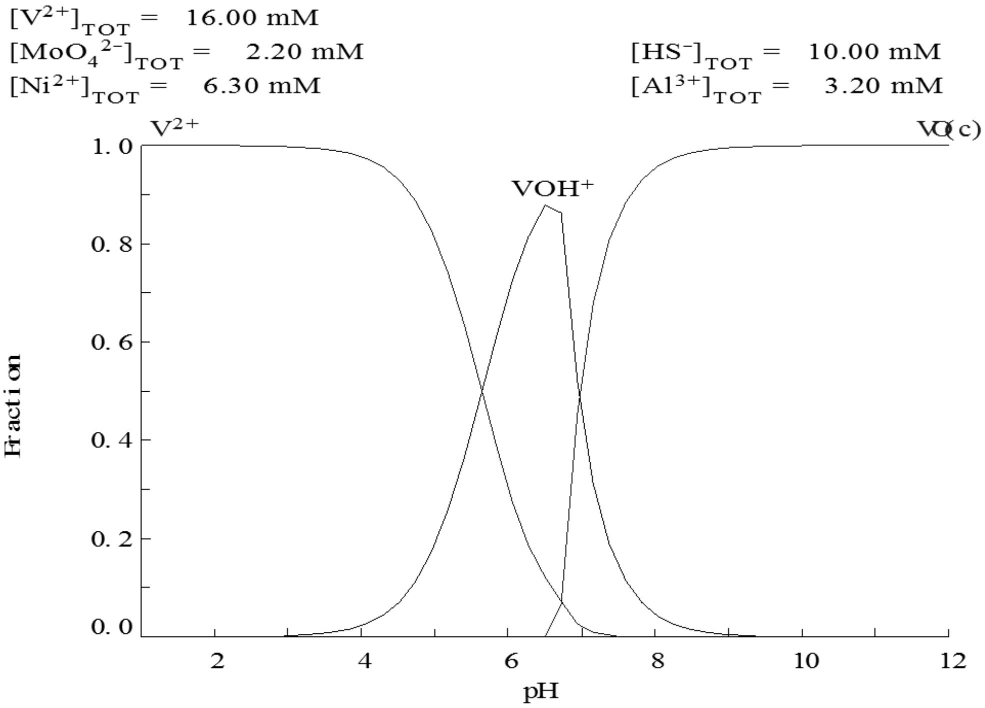


Figure 11.5 Chemical speciation diagram of vanadium (bioleach liquor).

As reported in figure 8.5 and 11.5 both aluminum and vanadium do not form sulfide compounds but they are removed only as hydroxide and oxide compounds, while molybdenum and nickel in presence of a sulfide source are precipitated as sulfide metal compounds (figure 9.5 and 10.5).

As showed by Medusa speciation diagrams, varying the pH values is possible obtain a selective precipitation of all four metals investigated; the aluminum, strong flocculating agent can be precipitated at pH 4 as hydroxide compound, molybdenum and nickel as sulfide compounds at pH 0.5 and 3.5 respectively and vanadium as oxide compound at pH values more than 6.

5.1.4 Preliminary precipitation experiments in presence and absence of sodium sulfide

In order to find a right path for a selective precipitation of base metals present into the spent refinery catalysts has been conducted several experiments to check the behavior of metals investigated at the varying of pH values in presence and absence of sodium sulfide (fig 12.5 and 13.5 respectively).

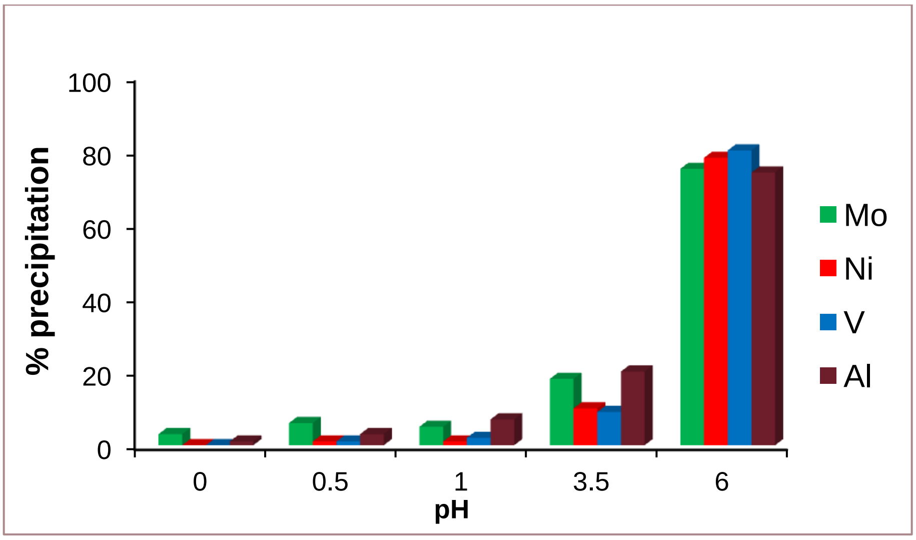


Figure 12.5 Precipitation of base metals investigated at different pH values (bioleach liquor).

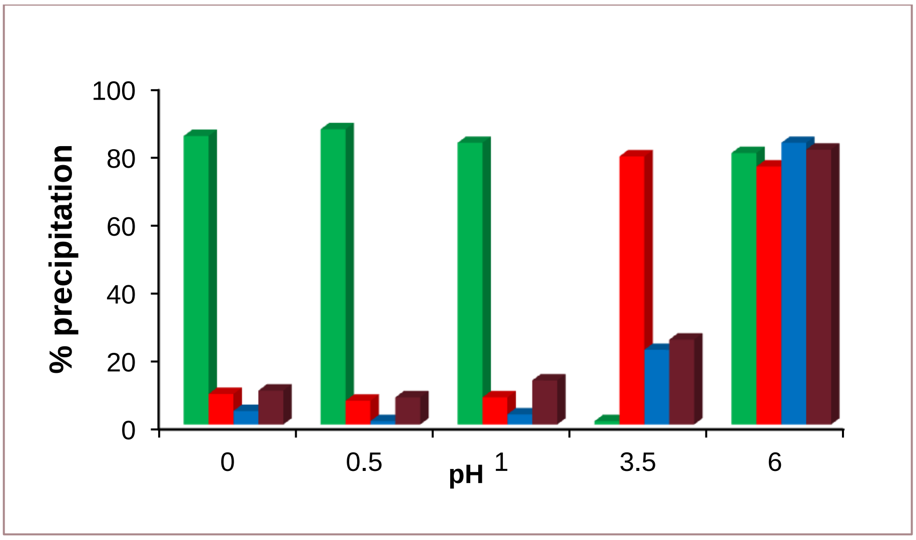


Figure 13.5 Precipitation of base metals investigated at different pH values in presence of sodium sulfide (bioleach liquor).

As reported in figure 12.5, molybdenum, nickel, vanadium and aluminum do not precipitate before the pH 3.5 value in absence of sodium sulfide, while at pH 6 the precipitation was simultaneous for all four metals investigated. These results are in accordance with the experimental results obtained with direct precipitation mechanism (see fig. 4.5); therefore from pH 6 the all four metals were precipitated also in absence of sulfide source. In figure 13.5 instead are reported the percentages of precipitation of base metals in presence of sodium sulfide (1 g/L was added in synthetich bioleach liquor and 10 g/L in synthetic leach liquor); the molybdenum in presence of sodium sulfide at strong acid pH values (from zero to 1) react with S and precipitate as sulfide compound while nickel, aluminum and vanadium do not precipitate; settling the pH at 3.5, occurred the selective precipitation of nickel as sulfide compound while at pH 6 occurred the simoultaneous precipitation of all rest of metals remained in solution. In this way, the removing of aluminum before all of four metals at pH 4, permit a selective precipitation of molybdenum at pH 0-1 and nickel at pH 3.5 as sulfide compounds and at the end the precipitation of vanadium at pH 6 as oxide compound. These experiments has been conducted also using synthetic leach liquor solutions (data not shown) confirming that is possible a selective precipitation of aluminium, molybdenum, nickel and vanadium in order to obtain “preconcentrate products” rich in aluminium when the precipitation occurred at pH 4, rich in molybdenum when the precipitation occurred at pH 0-1, rich in nickel at pH 3.5 and rich in vanadium at pH 6.

5.1.5 Selective precipitation of base molybdenum, nickel, vanadium and aluminum by adding of sodium sulfide

Based on the preliminary chemical speciation studies conducted with Medusa software and subsequently precipitation tests done in presence and absence of sodium sulfide, the scheme proposed for the selective recovering of base metals provides the precipitation of aluminum (pH 4) before the molybdenum (pH 0.5), nickel (pH 3.5) and vanadium (pH 6).

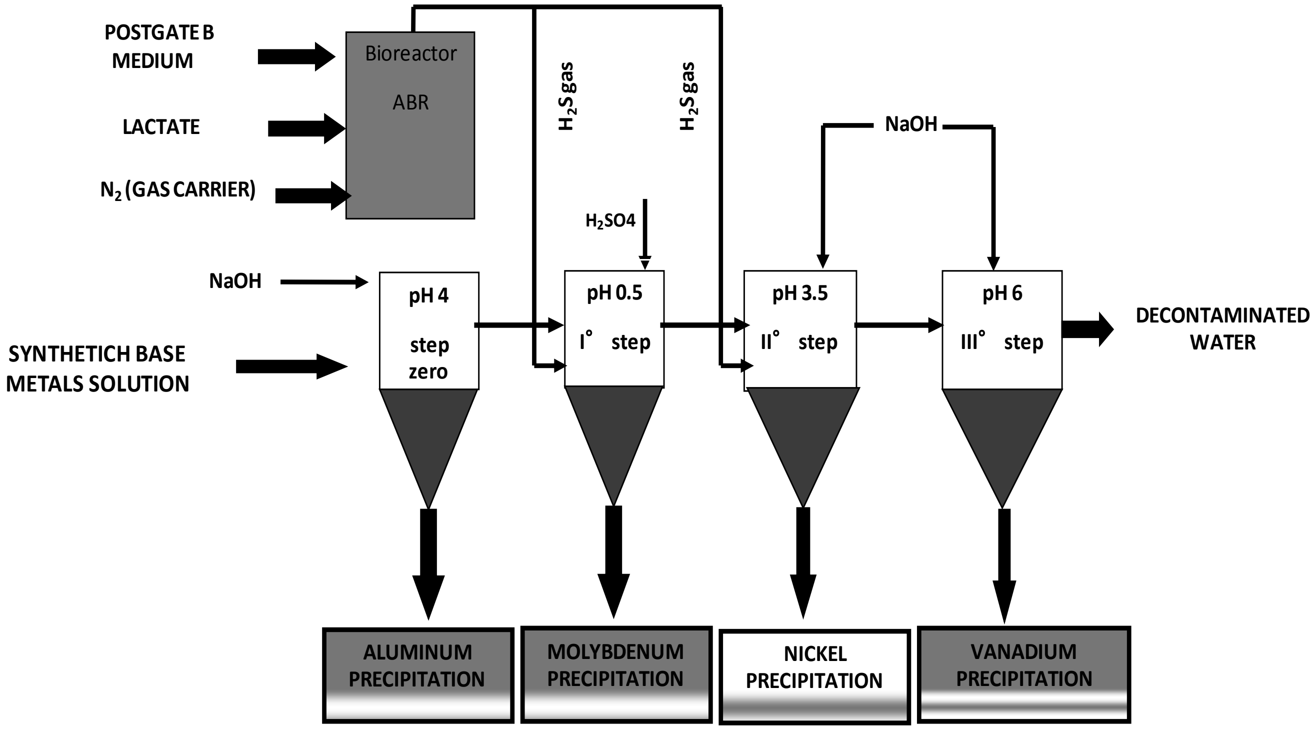


Figure 14.5 Scheme of selective recovery of base metals at different pH values.

Since that the presence of aluminum have adversely effects on the selective precipitation of other metals was removed before at all metals by adding of sodium hydroxide at pH 4. In figure 15.5 and 16.5 are reported the comparisons of percentages of precipitation of base metals (synthetic leach liquor) when the aluminum was removed after molybdenum and nickel (fig. 15.5, test A) and when was removed before at all other metals (fig. 16.5, test B)

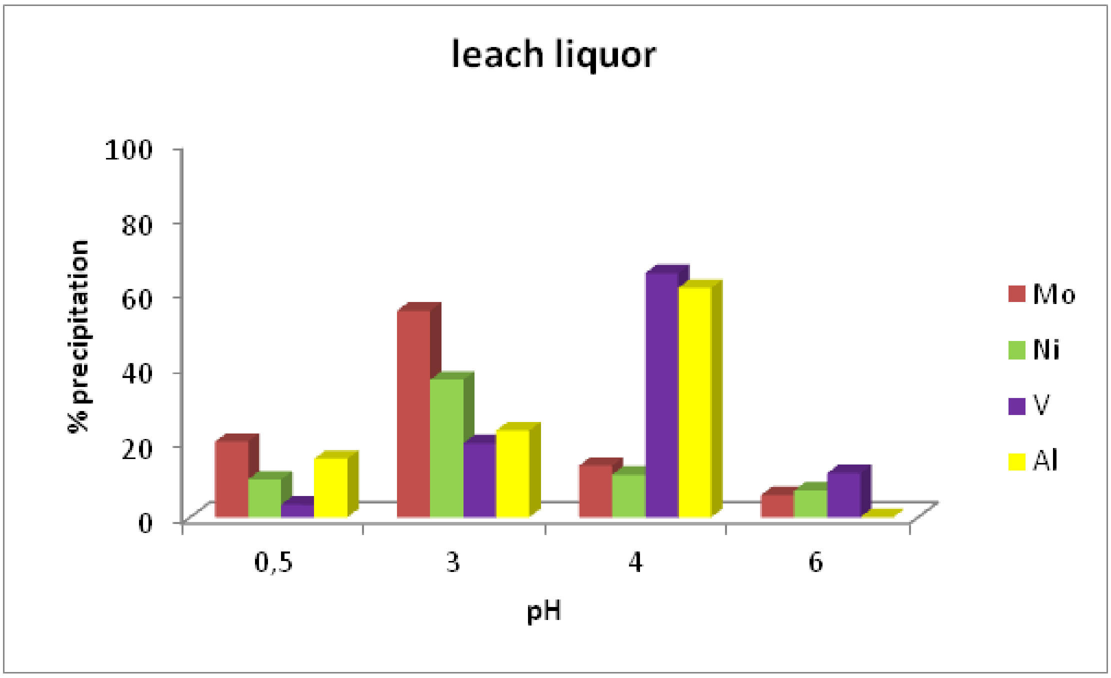


Figure 15.5 Percentages of precipitation with aluminum precipitated after molybdenum and nickel (test A).

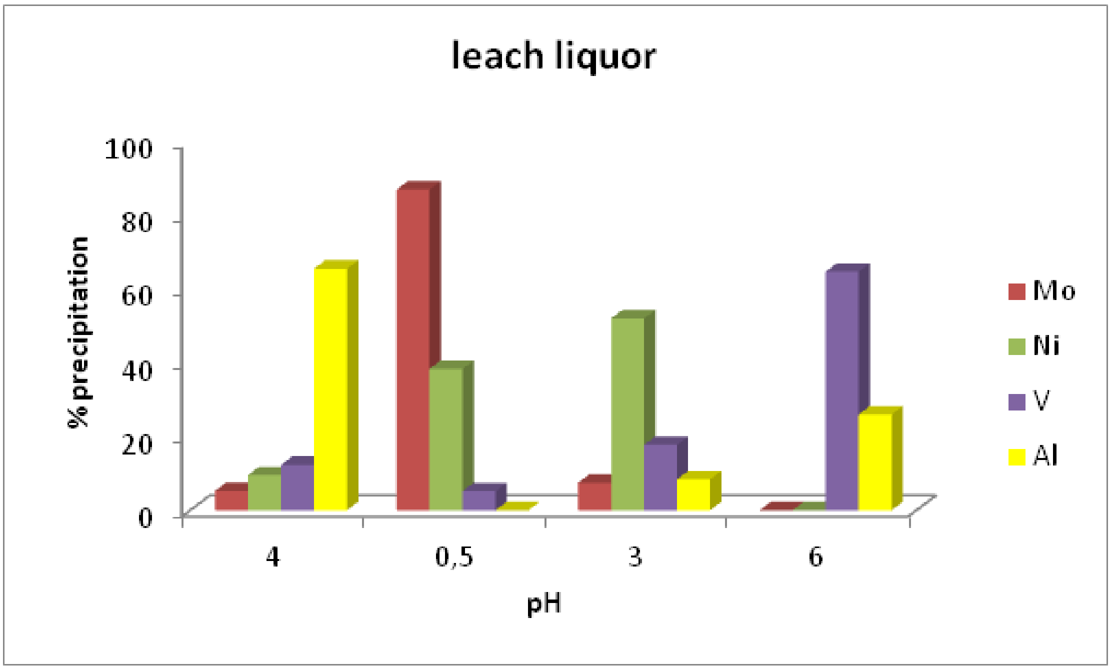


Figure 16.5 Percentages of precipitation with aluminum precipitated before at all other metals (test B).

The presence of aluminum have adversely effects on the selective precipitation due to its flocculating strong capacity; for this aspect is better remove the aluminum before at all other metals increasing the pH up to 4 and then decreasing the pH up to 0.5 to obtain the precipitation of molybdenum as MoS.

As shown in figure 15.5 and 16.5 the percentage of precipitation of molybdenum was very low in the test A, while in the test B it was around 90%; moreover, the presence of aluminum at pH 4 cause the co-precipitation of vanadium (up to 60%, see fig 15.5), while when the aluminum was removed before (test B), the co-precipitation of vanadium at pH 4 was only around 15%.

5.1.6 Selective precipitation and purity degrees of the precipitates obtained by sodium sulfide adding

The selective precipitation step by step of base metals has been made utilizing two synthetic base metals solutions prepared to simulate the liquors obtained from leaching and bioleaching processes of spent refinery catalysts; the solutions 1 and 2 were prepared in according with leaching experiments conducted by Ferella et al (2011) and bioleaching experiments conducted by Beolchini et al (2009) respectively (see table 1.5).

	Al (M)	Mo (M)	Ni (M)	V (M)
Leach liquor(LC)	0.055	0.16	0.085	0.15
Bioleach liquor (LB)	0.0032	0.0022	0.0063	0.016

Table 1.5 Molar concentrations of base metals in synthetic leach liquor and bioleach liquor.

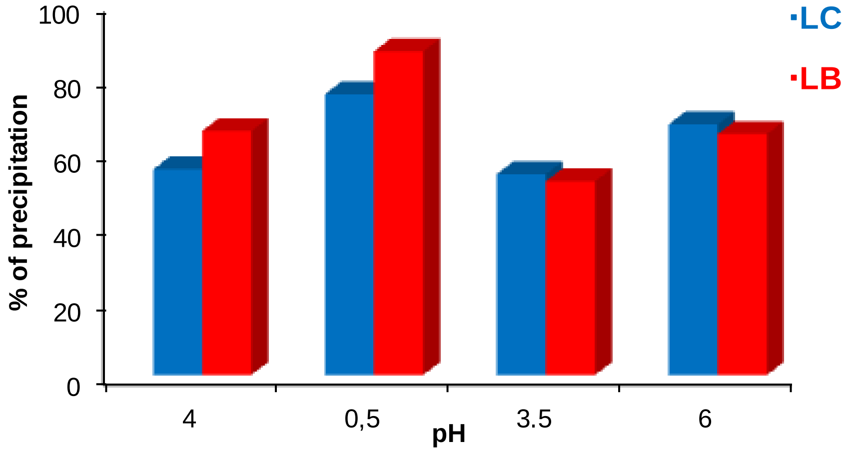


Figure 17.5 Comparison of precipitation percentages between synthetic leach liquor and bioleach liquor (are reported the precipitation percentages of aluminum at pH 4, molybdenum at pH 0.5, nickel at pH 3.5 and vanadium at pH 6).

As shown in fig. 17.5, the percentages of precipitation were not affected from the metals concentrations; both for bioleach and leach liquors, the precipitations were over 80% for molybdenum, 60% for nickel and 70% for vanadium.

The composition of precipitates obtained were determinated considering the amount (mg) of metal target precipitate (for example the molybdenum was the metal target at pH 0.5) on the amount (mg) of all four metals investigated.

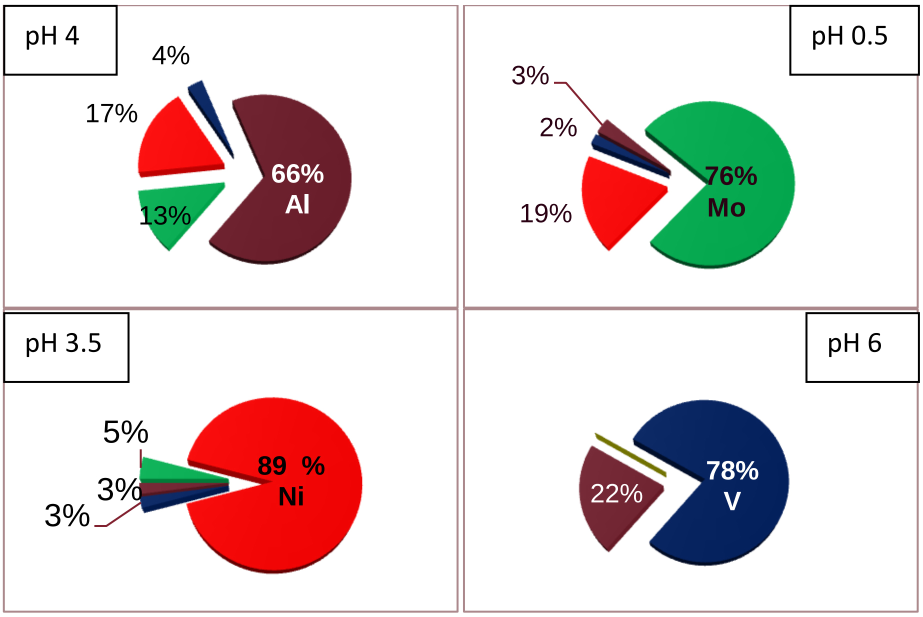


Figure 18.5 Composition of precipitates obtained at pH 4, 0.5, 3.5 and 6 (synthetic leach liquor solution).

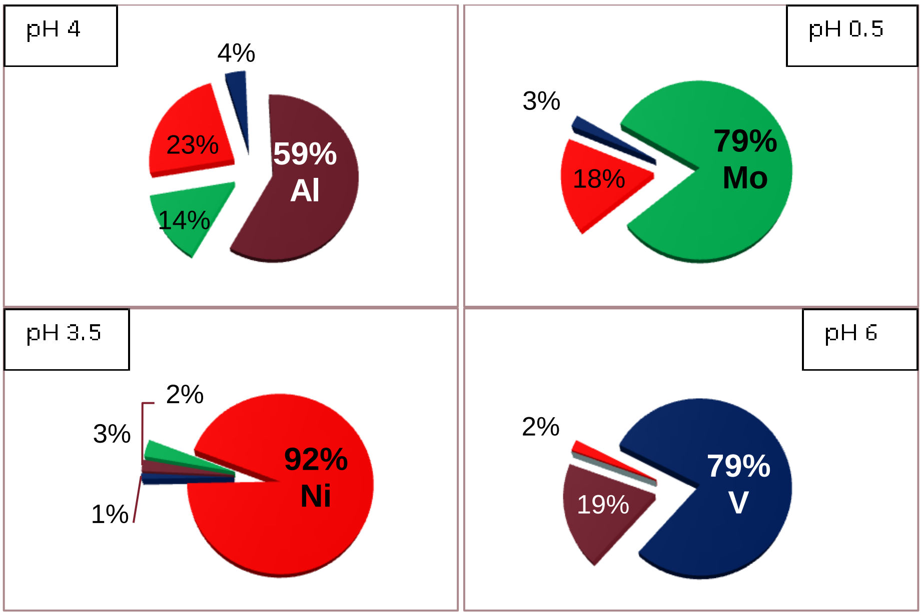


Figure 19.5 Composition of precipitates obtained at pH 4, 0.5, 3.5 and 6 (synthetic bioleach liquor solution).

As shown in fig. 18.5 and 19.5, the precipitates obtained had a high degrees of metals target; in particular both for leach liquor and bioleach liquor the amount of molybdenum, nickel and vanadium in the precipitates obtained at pH 0.5, 3.5 and 6 respectively were greater than 75%.

5.1.7 Selective precipitation of molybdenum, nickel and vanadium from synthetic base metals solution with H_2S gas produced by sulfate reducing bacteria in an lactate-fed anaerobic baffled reactor

Sulfate-reducing anaerobic baffled reactor (ABR) fed with lactate was operated continuously at room temperature for 70 days to evaluate sulfate reduction and hydrogen sulfide production capacity along with the possibility to precipitate base metals from synthetic leach and bioleach liquors.

Figure 20.5 Photograph of anaerobic baffled reactor (ABR).

The aim of this work was to evaluate the feasibility of a sulfidogenic anaerobic baffled reactor (ABR) for the production of hydrogen sulfide for the selective precipitation and recovery of metal sulfides from a synthetic heavy metals solution containing molybdenum, nickel, cobalt and vanadium in a separate unit process. These four base metals are present onto spent refinery catalysts that have been classified as hazardous solid wastes by the United States Environmental Protection Agency (USEPA). The bioleaching of the metals from the catalyst followed by selective precipitation with biogenic H_2S could allow the recovery of the metals from the wastes.

The sulfate reducing anaerobic baffled reactor (ABR) had four chambers and a total liquid volume of 28 L (PFWA, plastic fabrications WA) (Figure 20.5).

The ABR was operated as base metals synthetic solution treatment system on period of 70 days. Biogenic H_2S gas produced from SRB was sent in another chemical precipitation reactor by N_2 gas carrier in order to obtain the selective precipitation of molybdenum at pH 0.5, nickel and cobalt at pH 3.5 and vanadium at pH 6. The N_2 carrier gas was blown from the bottom and carries with it the H_2S gas produced from the bacteria; the gas mixture was escaped from the top of bioreactor by sampling port and sent in the precipitation reactor where occurred the heavy metals precipitation.

The bioreactor was operated in continuously and the removal of sulfate, H_2S dissolved produced, pH, ORP, total alkalinity and TOC were monitored three times per week.

Sulfate load was stepwise increased (see Fig. 21.5); the sulfate reduction was negligible for the first ten day and after increased from 20% to about 50% within 70 days of continuous operation. The initially SO_4^{2-} influent concentration was 1.5 g/L, after 20 days was increased up to 2 g/L while the influent concentration of Lactate was 1.23 g/L.

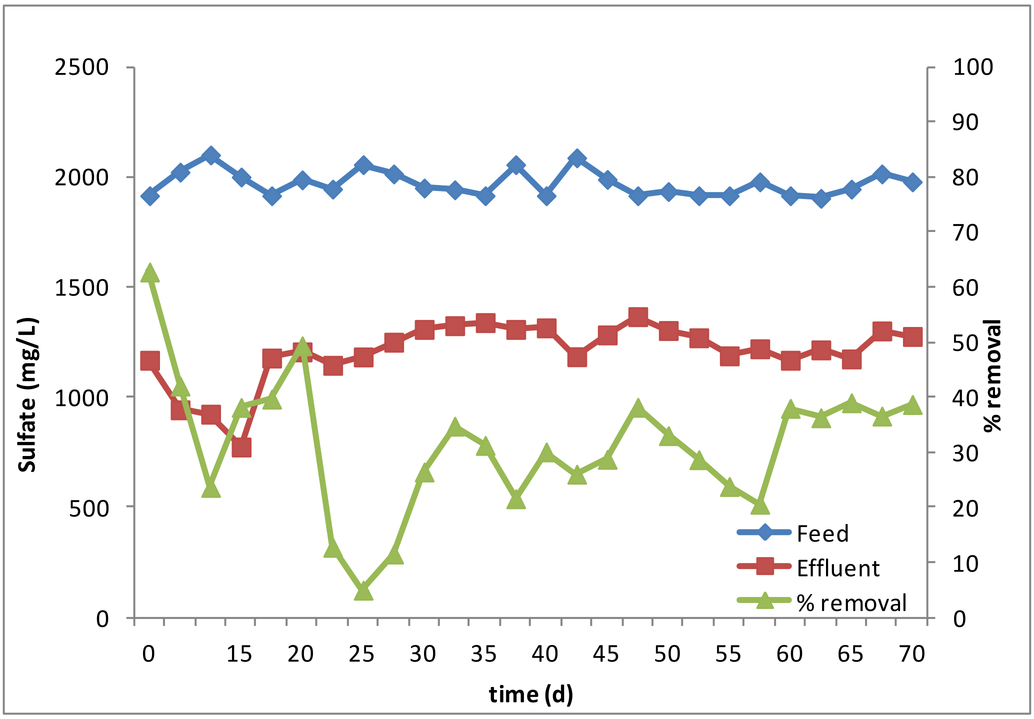


Figure 21.5 Feed and effluent concentration and sulfate removal.

The quantity of H_2S produced was within the range of 100-455 mg/L (see fig 22.5), reaching an average steady value of 250 mg/L after around 40 days.

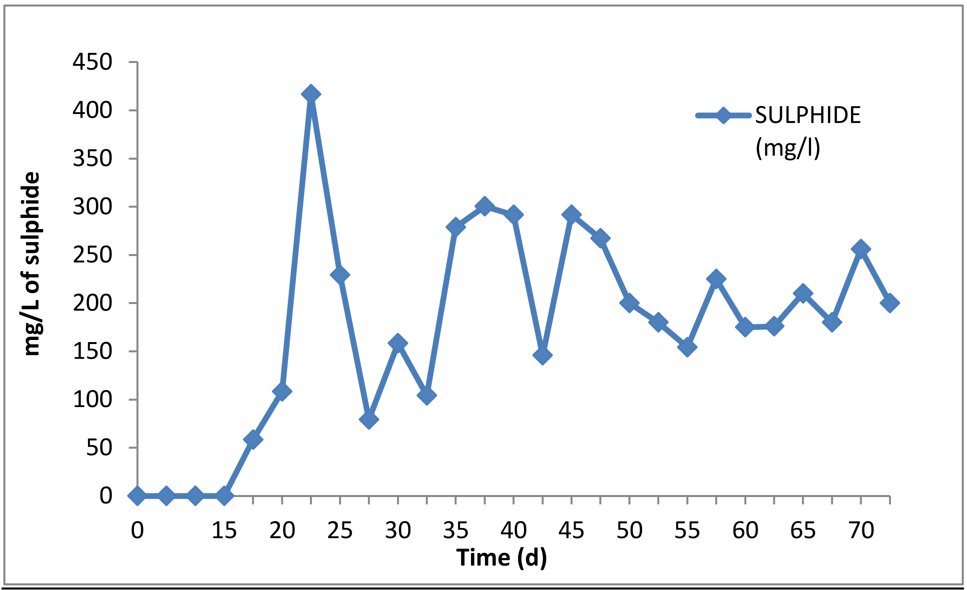


Figure 22.5 Dissolved sulfide concentration in the bioreactor.

Maximum sulfate removal rate was 181 mg/SO_4^{2-} L d at the end of experiment period while the maximum sulfate-loading rate during the experiment was 429 mg/H_2S L d (effluent value) (see fig 23.5). During the experiment, pH and Eh were monitored to check the bacteria activity; the ABR pH was 7-7.7 on all period of the experiment; the Eh values were stable within the range of -200/-350 mv establishing a strongly reducing environment inside the reactor (see fig 24.5 and 25.5). The strong reducing conditions inside the bioreactor permitted to the sulfate reducing bacteria to reduce the sulfate to sulfide (H_2S gas) that then it was sent in separated precipitation reactor for the precipitation of base metals. The reduction of dissolved total organic carbon (fig 26.5) resulted to be very high during all time of experiment reaching the maximum reduction value of 88%. In fig 27.5 are reported the mg/L of $CaCO_3$ present in the influent and in the effluent of bioreactor; the increasing of total alkalinity in the effluent is another parameter that indicates the sulfate reducing bacteria activity is going on because, in according with the following equation, the bacteria form HCO_3^- which reacts with ion H^+ for give carbon anhydride.

$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$

where CH_2O=organic substrate (electron donor)

$H_2S + M^{2+} \rightarrow MS(s) + 2H^+$

where M^{2+}= the metal cation

$HCO_3^- + H^+ \rightarrow CO_2(g) + H_2O$

Loading rate and removal rate have been calculated as reported in the following equations:

Loading rate = c_inf / HRT

where HRT is in days
V = reactor liquid volume (L)
Q = influent flow rate (L/d)
hydraulic retention time HRT = V/Q

Removal rate = (c_inf - c_eff) / HRT

where
c-inf = influent concentration (mg/L)
c-eff = effluent concentration (mg/L)

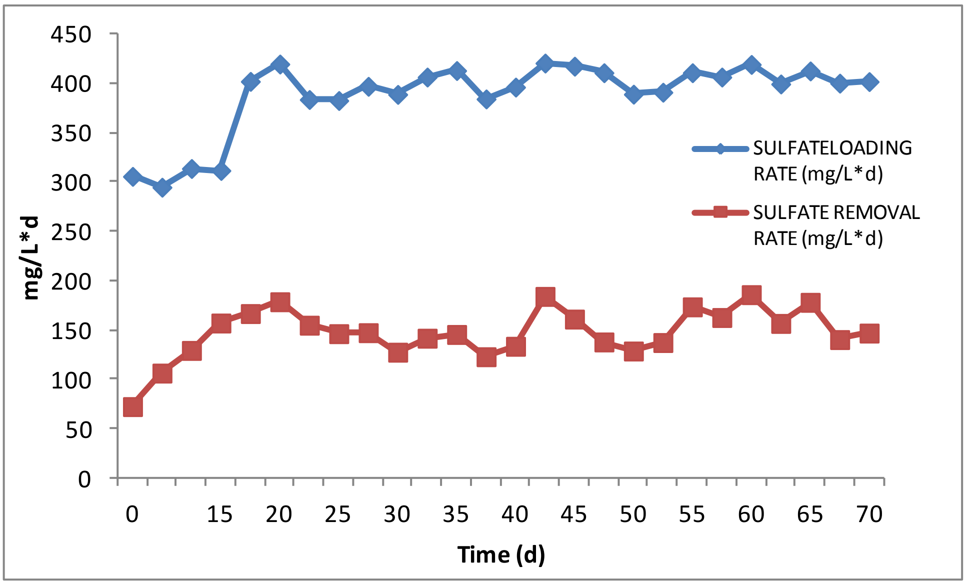


Figure 23.5 Comparison between sulfate loading rates and sulfate removal rates**.**

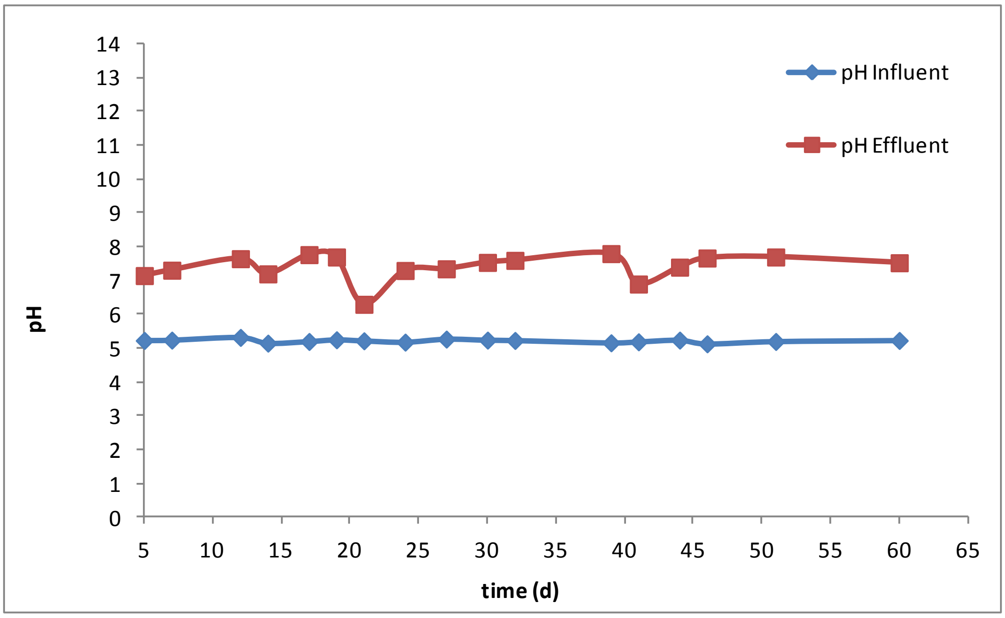


Figure 24.5 Influent and effluent pH values.

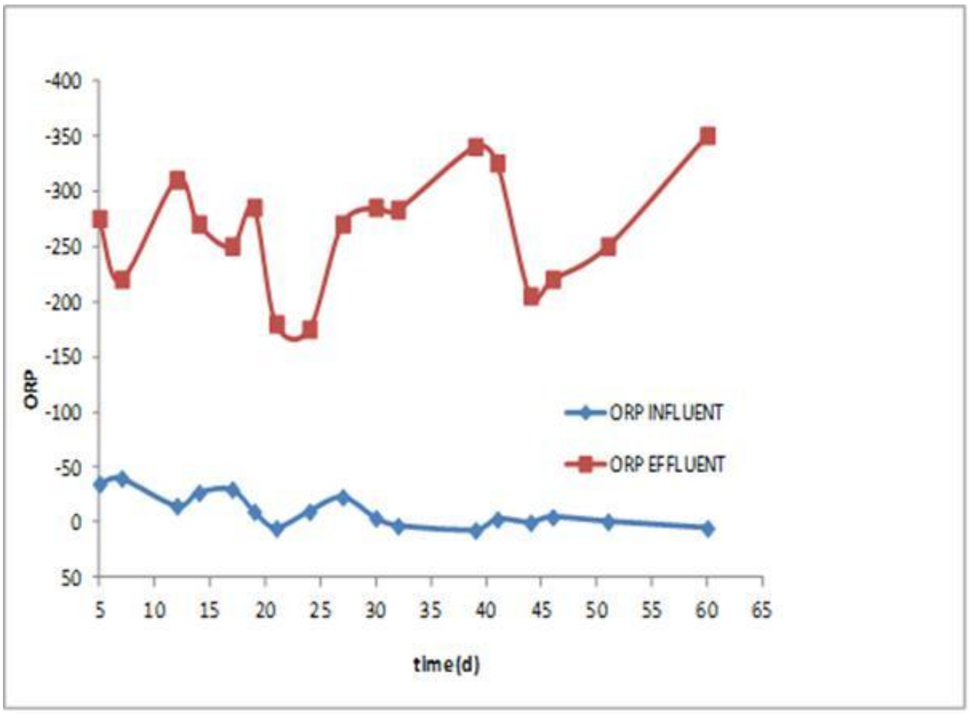


Figure 25.5 Influent and effluent ORP values.

Effluent ORP values established a reducing environment due to metabolic activities of sulfate reducing bacteria inside the bioreactor.

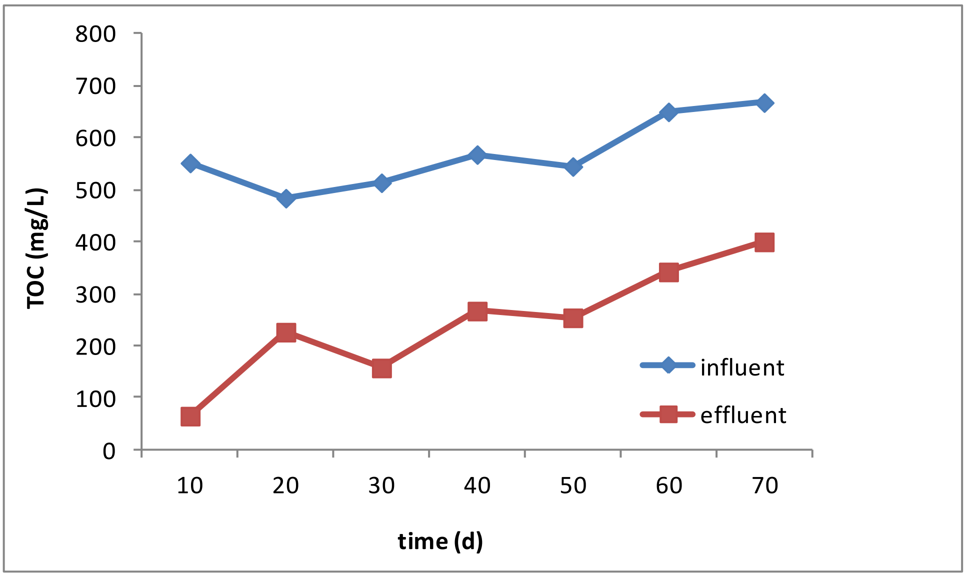


Figure 26.5 Influent and effluent TOC; the amount of total organic carbon (TOC) in the effluent was always less than of influent concentration due to the oxidation by sulfate reducing bacteria.

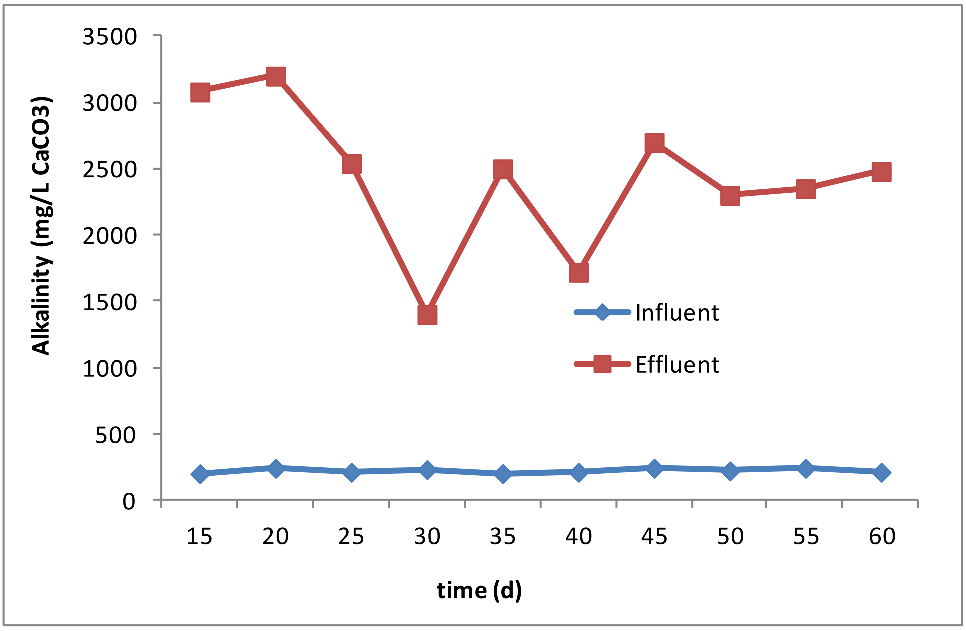


Figure 27.5 Influent and effluent alkalinity.

In table 2 are reported all bioreactor parameters investigated (medium values) during the experiment. All parameters reported were to assess the conditions of bioreactor and the bacteria activities. The pH and ORP values indicated that inside the reactor the rights growing conditions of sulfate reducing bacteria were established. Alkalinity produced and the reduction of TOC in the effluent respect of influent meant the carbon source was oxidized by bacteria.

Medium values	pH	ORP	Alkalinity (mg/L)	sulfate reduction (%)	TOC (mg/L)	sulfide dissolved (mg/L)	sulfate concentration (mg/L)	Sulfate removal rate (mM/L*d)	Sulfate loading rate (mM/L*d)
influent	5.20 (± 0.04)	-10 (± 10	220 (± 20)		570 (± 70)		1900 (±160)		
effluent	7.40 (± 0.30)	-260 (± 50)	2430 (± 330)		240 (± 90)		1040 (±150)		
reactor				30 (± 10)		250 (± 30)		0.90 (± 0.20)	1.00 (± 0.70)

Table 2.5 Medium values summary parameter of bioreactor investigated. All parameters reported shows the bacteria activities and sulfide production.

5.1.8 Metal removal with H_2S gas produced by sulfate reducing bacteria in an lactate-fed anaerobic baffled reactor

In the table 3.5 are showed all precipitation tests conducted with the respective percentages of precipitation at different step investigated. The molybdenum precipitation increased from 36% to 72% for the solution 1 (synthetic leach liquor) and for the solution 2 (synthetic bioleach liquor) at pH 0.5 respectively. The nickel concentration did not adversely effects on the precipitation at pH 3.5. Vanadium precipitation occurred as oxide metal by adding of NaOH at pH 6; for all three solutions investigated the percentages of precipitation were 67%, 64% and 68% for solution 1, 2 and 3 respectively.

	pH values	Mo (% prec.)	Ni (% prec.)	V (% prec.)
Solution 1	**0.5**	36	12	0
Solution 2	**0.5**	63	1	0
Solution 3	**0.5**	72	1	3
Solution 1	**3.5**	0	6	3
Solution 2	**3.5**	6	23	7
Solution 3	**3.5**	27	6	3
Solution 1	**6**	0	10	67
Solution 2	**6**	10	52	64
Solution 3	**6**	8	2	68

Table 3.5 Percentages of precipitation obtained at different pH values investigated for solution 1, 2 and 3.

The selective precipitation scheme proposed in according with preliminary speciation studies conducted with medusa software on molybdenum, nickel, cobalt and vanadium are showed in Fig 28.5. The molybdenum was precipitated as sulfide metal at pH 0.5 while vanadium was precipitated as hydroxide metal at pH 6. Regarding the molybdenum, the precipitation increased from solution 1 to solution 3 reaching the 72% of precipitation indicating that for molybdenum the sulfide precipitation was correlated with the heavy metal concentration; probably this less percentage of precipitation when the heavy metal concentration was higher was due to the less concentration of H_2S gas produced from the bioreactor (0.005 M) respect the base metal concentration contained in synthetic solution (see table 4.5). The vanadium precipitations for all three solutions investigated were very similar and exceed the 65% indicating that in the case of hydroxide/oxide precipitation by NaOH concentrated, the range of base metal concentration used had not adverse effects on precipitation. Nickel precipitation at pH 3.5 was not correlated with their initially concentration in solution and the percentage of precipitation did not exceed the 50%.

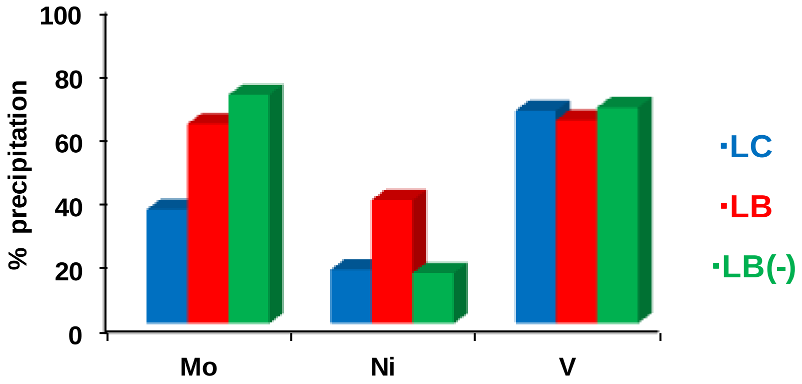


Figure 28.5 Percentages of precipitation of all metals investigated (solution 1, 2 and 3); for molybdenum are reported the percentages of precipitation obtained at pH 0.5, for nickel at pH 3.5 and for vanadium at pH 6.

	Mo [M]	Ni [M]	V [M]
Solution 1 (leach liquor - LC)	**0.029**	**0.079**	**0.12**
Solution 2 (bioleach liquor - LB)	**0.022**	**0.006**	**0.016**
Solution 3 [bioleach liquor (–)]	**0.0004**	**0.001**	**0.0019**

Table 4.5 Synthetic leach and bioleach liquor (molar concentration).

As reported in figure 22.5, after 50 days the system reached the steady state where the average production of H_2S dissolved into the bioreactor was around 200-250 mg/L (5.9-7.3 mM). Nevertheless it should be considered that sulphidric acid undergoes two acid dissociations (reaction 1 and 2):

$$H_2S \overset{K_P1}{\rightleftarrows} HS^- + H^+ \qquad K_P1 = \frac{[HS^-]\,[H^+]}{[H_2S} \qquad {}_PK_1 = 6.99 \qquad (1)$$

$$HS^- \overset{K_P2}{\rightleftarrows} S^{2-} + H^+ \qquad K_P2 = \frac{[HS^-]\,[H^+]}{[H_2S]} \qquad {}_PK_2 = 17.4 \qquad (2)$$

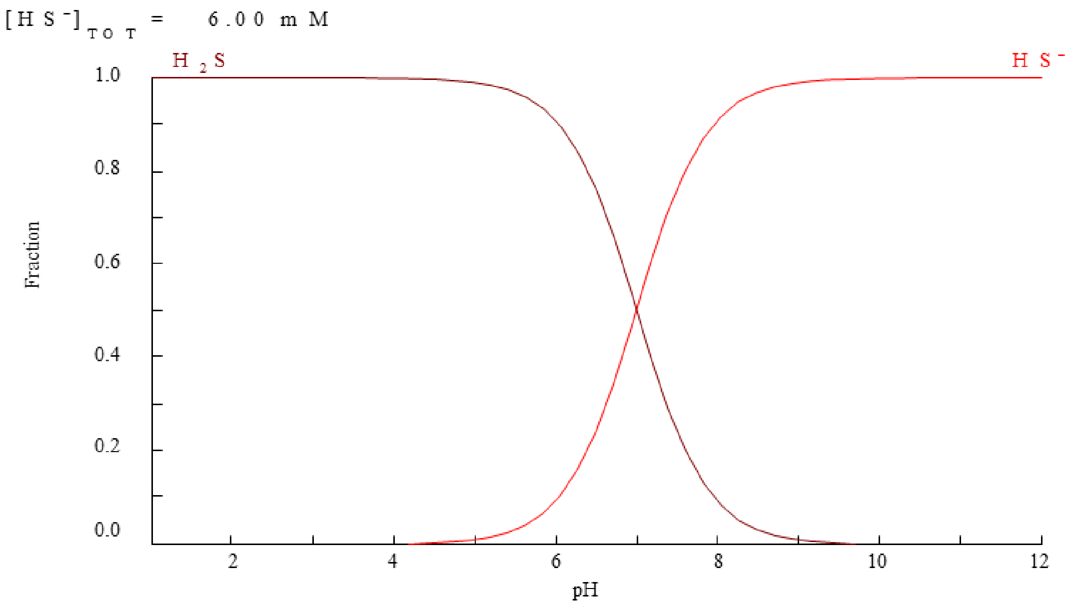


Figure 29.5 Chemical speciation diagram of H_2S by medusa software.

As shown in figure 29.5 at pH 7, at the same pH value of bioreactor, the fraction of H_2S gas is 50% while the other 50% is dissolved in solution as HS^- compound; this means that the maximum of H_2S that is possible to carry out from the bioreactor by N_2 gas carrier is half of total amount of H_2S dissolved measured by UV visible.

In addition even considering a quantitative transport of gas from bioreactor to precipitation reactor and from gas carrier to liquid phase, at pH 2 (pH of precipitation reactor) the predominant chemical species is H_2S gas which makes the reaction unfavorable due to gas escaping from the reactor; the amount of HS^- dissolved is negligible (see fig. 29.5) negatively affecting the precipitation of molybdenum when the synthetic solution used has a high metals concentration. Increasing the pH value the HS^- dissolved increase and the reaction is more favored. When low base metals concentration solutions are used the precipitation degrees increased as in the case of solution 2 and 3. In order to improve the capacity of precipitation by sulfide produced by anaerobic baffled reactor containing sulfate-reducing bacteria needs to increase the amount of H_2S gas by a higher sulfate reduction, increase the amount of bacteria inside the reactor and keep on the anaerobic reactor at least 250-300 in lab scale.

Despite the problem occurred with synthetic high concentrated metal solutions about the quantity of precipitation of molybdenum and nickel, the selective precipitation of base metals investigated showed in Fig. 28.5 suggest that is possible to obtain precipitates with high purity indices from synthetic solutions containing different metals by the reaction with H_2S gas produced from sulfate reducing bacteria.

The purity indices has been calculated in according with the following equation:

Precipitate pure degree= mg*(prec.)/mg tot

Where

mg*(prec)= mg of single metal precipitated at one specific pH value (e.g. 0.5, 3.5, 6);

mg tot= total mg precipitated of all four metals at one specific pH value (e.g. 0.5, 3.5, 6);

As shown in fig. 30.5 the precipitates purity indices of molybdenum, nickel and vanadium in solution 1 were in the range of 55-66%; these low purity indices were due to high base metals concentration in solution1 and were not able to obtain a high selective precipitation. In the case of solution 2 and 3 as showed in figure 31.5 and 32.5 respectively, the molybdenum and vanadium purity indices were 0.90 and 0.98 and 0.69 and 0.7 respectively; about the nickel the purity indices increased from solution 1(0.55) to solution 3 (0.7). The purity indices increased from solution 1 to solution 3 suggesting that the base metals concentration in solution 1 had an adversely effects.

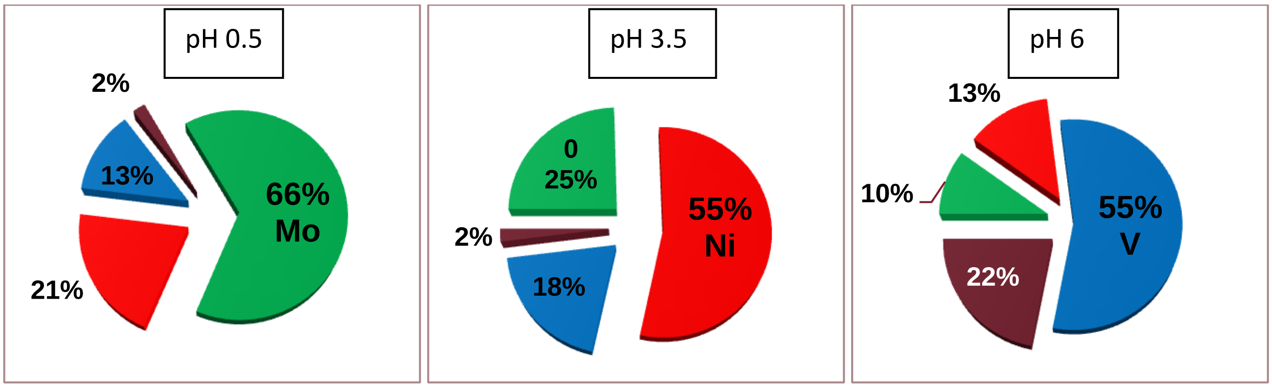


Figure 30.5 Composition of precipitates obtained at pH 0.5, 3.5 and 6 (synthetic leach liquor solution).

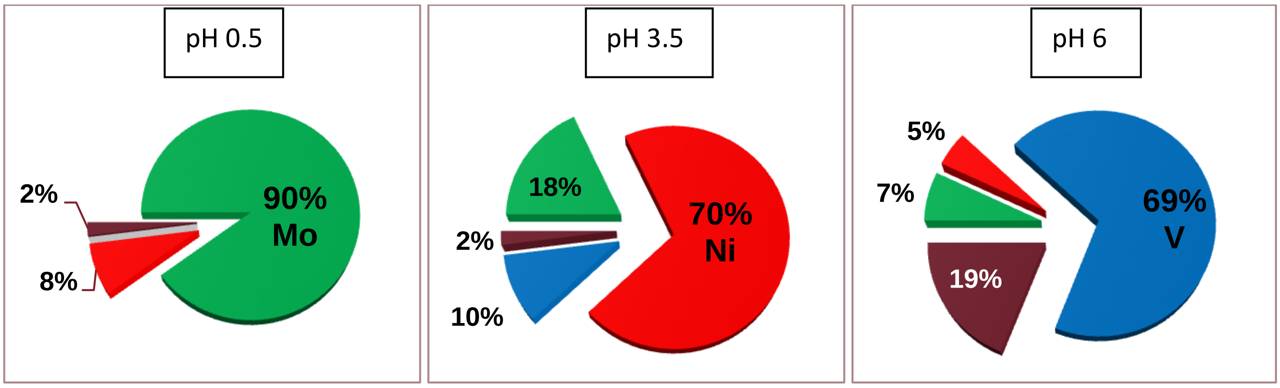


Figure 31.5 Composition of precipitates obtained at pH 0.5, 3.5 and 6 (synthetic bioleach liquor solution).

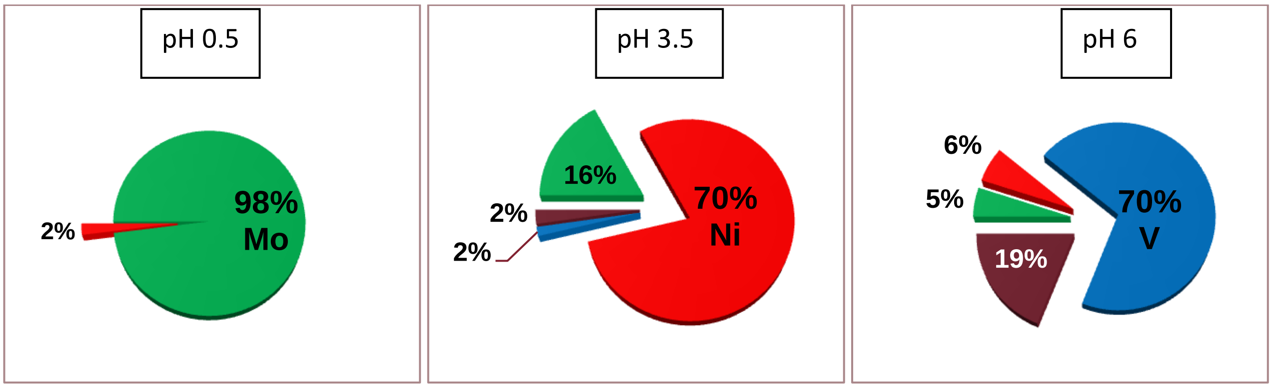


Figure 32.5 Composition of precipitates obtained at pH 0.5, 3.5 and 6 (synthetic bioleach liquor solution (-)).

5.1.9 Process analysis by Super Pro Designer: technical and economic preliminary studies

This paragraph shows the preliminary technical and economic analysis for the different spent catalysts treatment methods. The different spent catalysts treatment methods investigated are reported in table 5.5.

METAL EXTRACTION METHOD	**METAL RECOVERY METHOD**	**NAME OF SIMULATED PROCESSES**
CHEMICAL (ACID LEACHING)	**CHEMICAL** (PRECIPITATION BY Na_2S)	C-C
CHEMICAL (ACID LEACHING)	**BIOLOGICAL** (PRECIPITATION BY H_2S)	C-B
BIOLOGICAL (BIOLEACHING)	**BIOLOGICAL** (PRECIPITATION BY H_2S)	B-B
BIOLOGICAL (BIOLEACHING)	**CHEMICAL** (PRECIPITATION BY Na_2S)	B-C

Table 5.5 Different treatment methods investigated with Super Pro designer.

The preliminary study of technical and economical processes analysis has been conducted in order to evaluate the PBT (payback time), recovery of base metals, total recovery of matter and the production of liquid waste.

As shown in figure 33.5, the PBT decreasing when the amount per year of spent catalysts treated increased. Among the four processes investigated, the process C-C shown the lower PBT also when the simulation has done with 5000 tons/year and 2500 tons/year of spent catalysts treated. The simulating process C-B as was expected shown a PBT higher than other process because as reported in figure 28.5 and 30.5 the precipitation of base metals were lower than bioleach liquor (-) precipitation experiments; also the purity indices were lower than other precipitates obtained.

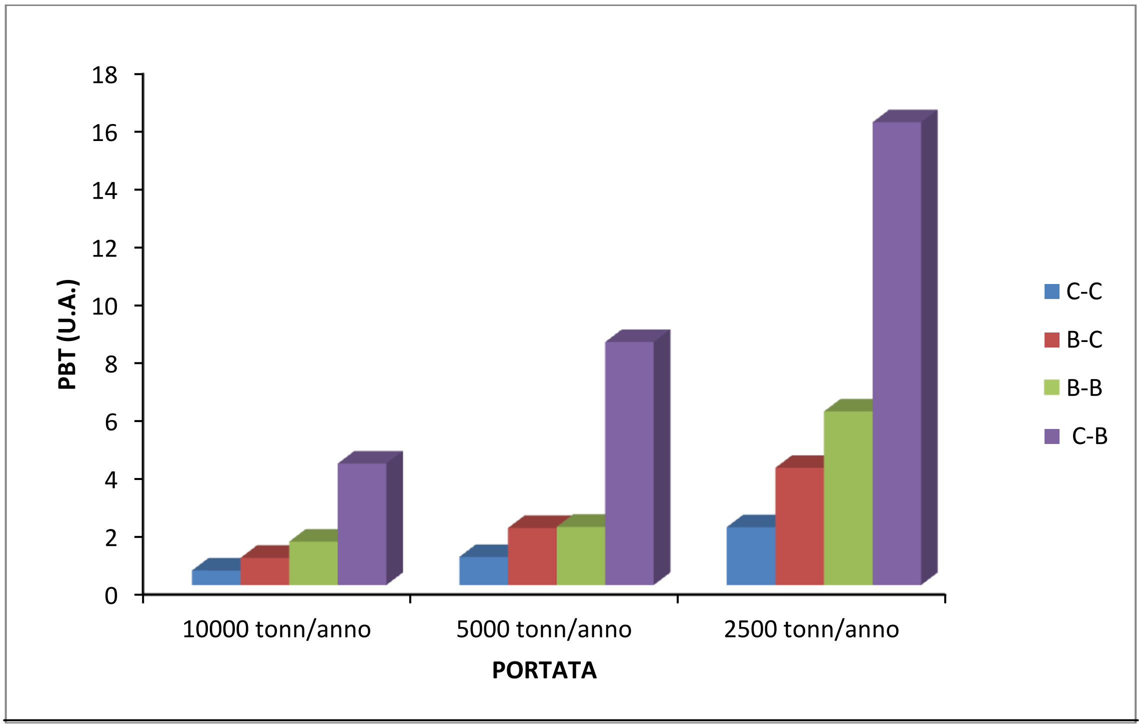


Figure 33.5 PBT of simulation processes investigated with Super Pro Designer.

Regarding the recovery of all base metals investigated the aluminum and vanadium percentages recovery were similar among the four different simulating processes studied; both base metals were precipitated as hydroxide and oxide compounds, while molybdenum and nickel recovery were strongly dependent from the production of H_2S gas. As shown in figure 34.5 a, the recovering of molybdenum and nickel were lower respect other processes simulated because the production of H_2S gas was not enough to precipitate the molybdenum and nickel present in leach liquor synthetic solution. The amount of aluminum recovered was for all four process at least 80% because was considered as metal recovery also the amount of aluminum present in the solid waste that formed after the leaching or bioleaching operation; in fact, the amount of aluminum in these solid wastes were always higher than 50%.

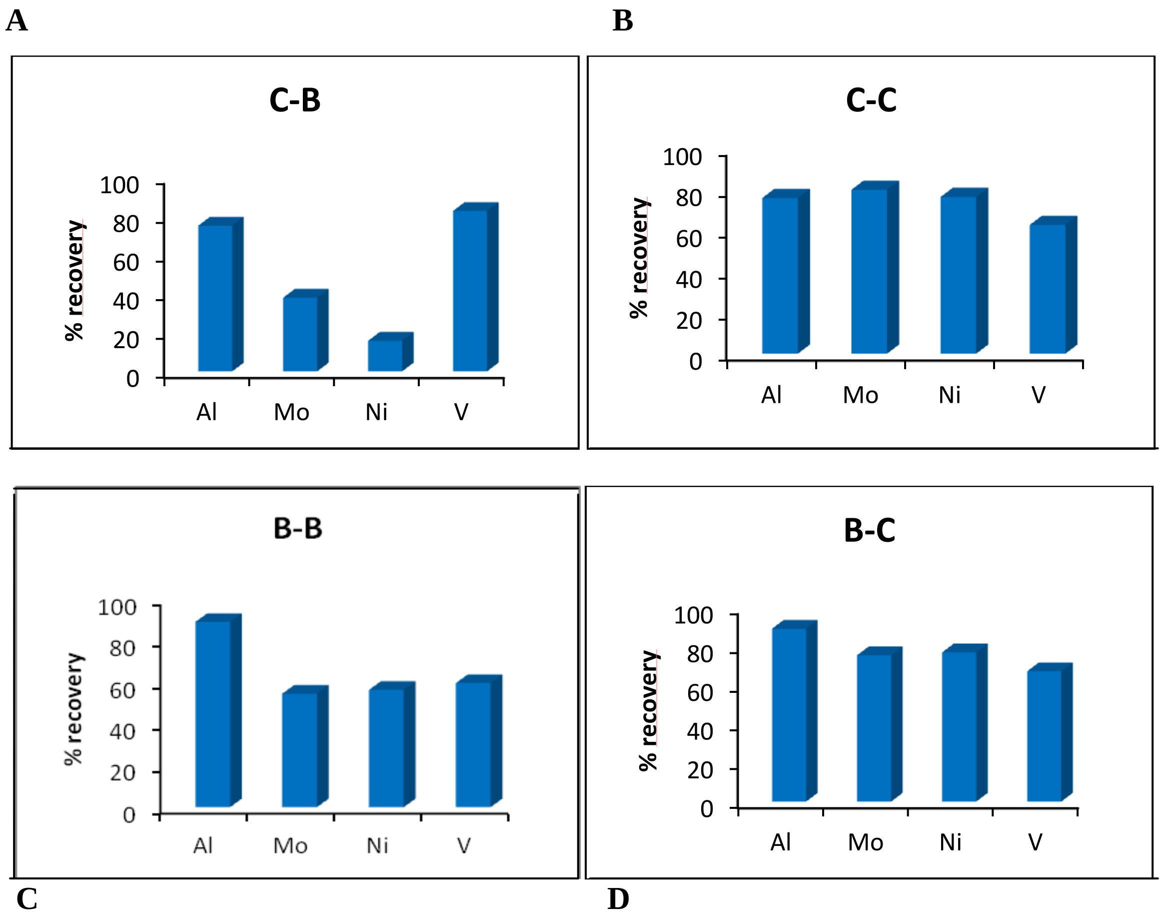


Figure 34.5 Percentages of base metals recovery.

The percentages of recovery has been calculated following the equation:

B/A*100

where
B= kg of target metal in the concentrated obtained
A= kg of target metal in the charged

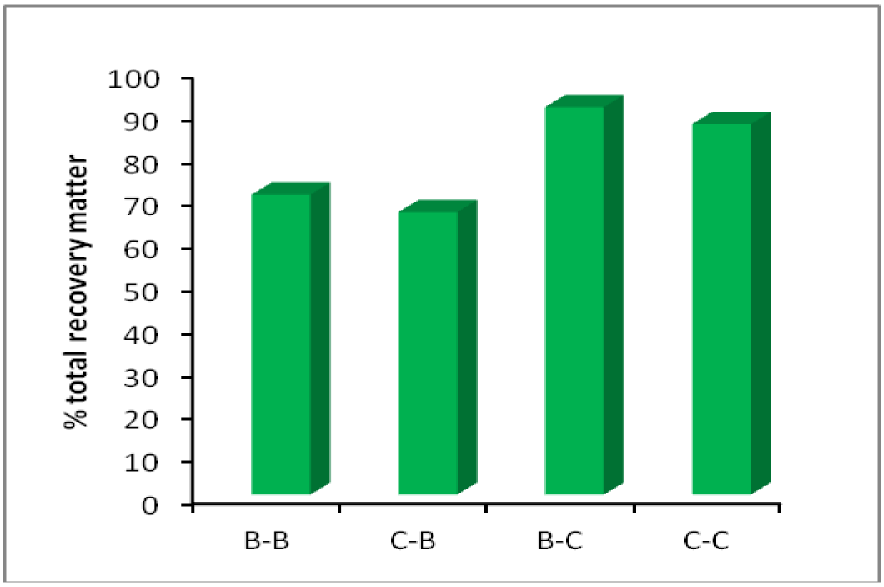


Figure 35.5 Total recovering of matter.

As shown in figure 35.5, the processes B-C and C-C showed a higher percentage of matter recovery while the both B-B and C-B processes were around 70% of recovery. The total recovery of matter was calculated following the equation:

X/C*100

where

X= total kg of compounds precipitated

C= total kg of compounds charged

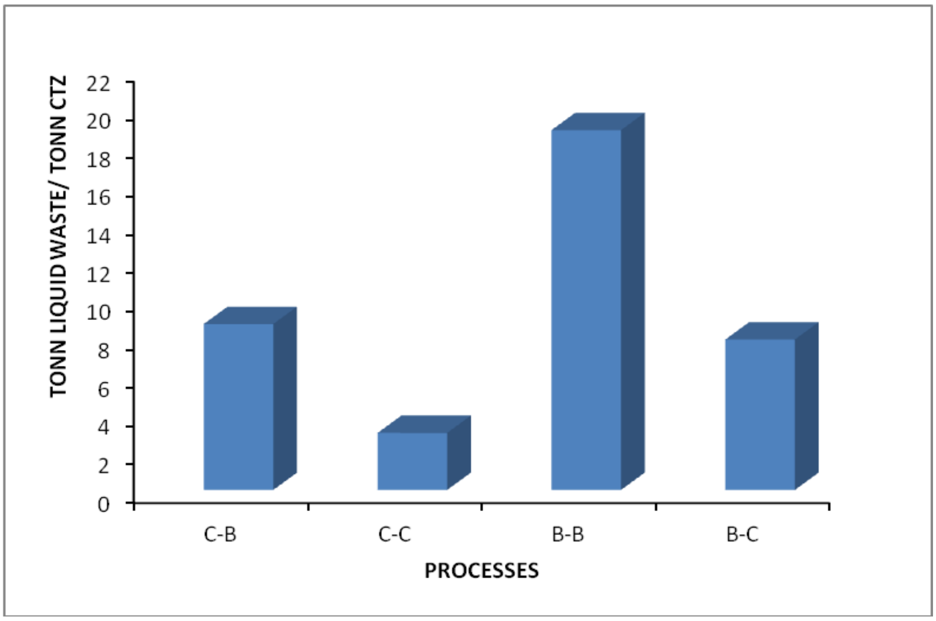


Figure 36.5 Amount of liquid waste generated.

As shown in figure 36.5, the liquid waste generated were less than 10 tons on 1 ton of spent catalysts treated for the process C-C, C-B and B-C while the process B-B was 19 tons on 1 ton of spent catalysts**.** The C-C process had a lower production of liquid waste, less than 4 tons for 1 ton of spent catalysts. The great production of liquid waste in the simulating process B-B was due to the liquid effluent derived from bioreactor and also for the water necessary for the bioleaching process.

CHAPTER SIX

CONCLUSIONS

Based on the results obtained and reported in this doctorate work, it can be concluded that the treatment of spent refinery catalyst by solubilization and subsequently sulfide precipitation is a valid alternative to other conventional treatments so far adopted; moreover, the processes proposed can be considered “environmental friendly processes” because the production of wastes is very limited.

The conclusions from the range of experiments conducted are as follows:

1) The indirect mechanism of precipitation prevents the inhibitory effects on SRB activity metabolic due to strong toxicity of base metals treated, moreover by indirect mechanism is possible to obtain a selective precipitation of all four metals investigated, thing not possible by direct precipitation mechanism.
2) The selective recovery process proposed is a valid path to obtain final concentrates with high purity degree of metals target: the amount of molybdenum in the precipitate obtained at pH 0.5 was 46%, nickel was 60% in the concentrated obtained at pH 3.5 and vanadium was 46% in the concentrated obtained at pH 6 (in the case was used a chemical leaching solution and the precipitation steps were made by adding of Na_2S).
3) The studies and analysis conducted on lactate-fed continuously ABR (anaerobic baffled reactor) demonstrated that is possible to validate in large part the results obtained by metals precipitation occurred with Na_2S mostly regarding the purity of precipitates obtained. About the capacity to precipitate the metal the ABR was more suitable to treat base metals solution with a low concentration such as bioleach liquor while with high concentrated base metals solution is preferable to use adding of Na_2S.
4) The treatment of high concentrate metals solutions like leaching solution were not satisfactory when the source of sulfide was produced by ABR reactor because the amount of H_2S gas produced was less than the metals concentration in synthetic solution; so consequently the precipitates obtained were less than precipitates obtained by the process where was used the Na_2S as precipitating agent but the purity indices were quite similar.

5) The simulating analysis processes made with Super Pro Designer showed a recovery of base metals higher than 70% reaching maximum values of 90% in the case of aluminum and molybdenum.
6) The liquid waste produced were less than 4 tons on 1 ton of spent catalysts treated with the process C-C and thing not less important, the solids compounds that were not leached were considered as aluminum concentrated because the percentages of aluminum was always higher than 50%; therefore for the four simulating analysis processes investigated, the amount of solid wastes were zero.
7) Among the different simulating processes done, the process C-C had the lower PBT; was the only process able to have PBT less than 4 years even when the amount of catalysts treated was 2500 tons; also the waste liquid generated was much lower than each other processes simulated and the quantity of metals recovered were higher than 80% for all four base metals investigated.
8) The concentrates obtained can be further refined to obtain commercial products like molybdenum trioxide or vanadium pentoxide; otherwise, the concentrates of molybdenum can be sell direct as rich-sulfide molybdenum concentrates (sulfide molybdenum is used as car lubricating oil), while nickel and vanadium are used to production of super alloy.

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APPENDIX A (PROCESS B-C)

```
EXECUTIVE SUMMARY                                     (2011 prices)
TOTAL CAPITAL INVESTMENT                               5510000  $
CAPITAL INV. CHARGED TO THIS PROJECT                   5510000  $
OPERATING COST                                         18503000  $/year
PROCESSING RATE                                        4997520  kg/year of S-125
UNIT PROCESSING COST                                   3.702  $/kg of S-125
TOTAL REVENUES                                         23746000  $/year
GROSS MARGIN                                           22.08  %
RETURN ON INVESTMENT                                   63.51  %
PAYBACK TIME                                           1.97  years
IRR AFTER TAXES                                         52.11  %
NPV (at 7.0 % interest)                                19567000  $
=====================================================
MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2011 prices)
=====================================================
Quantity/      Description                       Unit Cost     Cost
Stand-by                                            ( $ )        ( $ )
--------------------------------------------------------------------------
1/0  V-102     Continuously Stirred Reactor        19000       19000
Volume   = 2047.20 L
Diameter = 1.01 m
1/0  PFF-101   Plate & Frame Filter                64000       64000
Filter Area  = 22.50 m^2
1/0  V-103     Continuously Stirred Reactor        19000       19000
Volume   = 2021.83 L
Diameter = 1.01 m
1/0  PFF-102   Plate & Frame Filter                64000       64000
Filter Area  = 22.41 m^2
1/0  V-104     Continuously Stirred Reactor        19000       19000
Volume   = 2032.59 L
Diameter = 1.01 m
1/0  PFF-103   Plate & Frame Filter                64000       64000
Filter Area  = 22.68 m^2
1/0  V-105     Continuously Stirred Reactor        19000       19000
Volume   = 2035.07 L
Diameter = 1.01 m
1/0  PFF-104   Plate & Frame Filter                64000       64000
Filter Area  = 22.67 m^2
1/0  GR-101    Grinder                            20000       20000
Rated Throughput = 631.00 kg/h
1/0  V-106     Continuously Stirred Reactor        47000       47000
Volume   = 39372.29 L
Diameter = 2.72 m
1/0  PFF-106   Plate & Frame Filter                64000       64000
Filter Area  = 16.97 m^2
TOTAL EQUIPMENT PURCHASE COST                                  579000

FIXED CAPITAL ESTIMATE SUMMARY (2011 prices)
===================================================
A. TOTAL PLANT DIRECT COST (TPDC)             (physical cost)
1. Equipment Purchase Cost                  $        579000
2. Installation                                      352000
3. Process Piping                                    203000
4. Instrumentation                                   232000
5. Insulation                                        17000
6. Electricals                                        58000
7. Buildings                                         260000
8. Yard Improvement                                  87000
9. Auxiliary Facilities                              232000
                                          TPDC =     2019000
B. TOTAL PLANT INDIRECT COST (TPIC)
10. Engineering                                      505000
11. Construction                                     707000
                                          TPIC =    1211000
C. TOTAL PLANT COST (TPDC+TPIC)            TPC =    3231000
12. Contractor's fee                                 162000
13. Contingency                                      323000
(12+13) =                                                485000
====================================================
D. DIRECT FIXED CAPITAL (DFC)     TPC+12+13 =      3715000
====================================================
```

```
RAW MATERIALS COST SUMMARY
==============================================================
Raw                    Unit Cost    Annual Amount           Cost
Material                ( $/kg )          ( kg )          ( $/yr )      %
------------------------------------------------------------------------------------------
ion H+                 0.030        2496836.45         74905          0.60
Sulfuric Acid            0.070         188100.00         13167          0.11
Sodium Hydroxid        0.040          19016992.59      760680          6.13
sodium sulphur          0.300          887040.00         266112         2.15
sulfate ferric          0.500         22572000.00      11286000    91.01
-------------------------------------------------------------------------------------------
TOTAL                                   45160969.04        12401000   100.00
===============================================================
WASTE TREATMENT / DISPOSAL (2011 prices) b. LIQUID WASTE
=========================================================
Stream              Unit Cost        Annual Amount                   Cost
Name               ( $/kg )             ( kg )                        ( $/yr )
-------------------------------------------------------------------------------------
S-122             1.000e-001       43365736.71                     4337000
=========================================================
WASTE TREATMENT/DISPOSAL TOTAL COST (b)              4337000
=========================================================
UTILITY REQUIREMENTS (2011 prices) ELECTRICITY
-------------------------------------------------------------------------------
Procedure        Equipment            Annual Amount          Cost
Name              Name                 ( kWh )               ( $/yr )
-------------------------------------------------------------------------------
P-2             V-102                   79200                   7920
P-3             PFF-101                198000                 19800
P-4             V-103                 79200                     7920
P-5             PFF-102               198000                 19800
P-6             V-104                 79200                     7920
P-8             PFF-103               198000                 19800
P-9             V-105                 79200                     7920
P-10             PFF-104              198000                 19800
P-15             GR-101               499752                 49975
bioleaching       V-106                 79200                     7920
P-16             PFF-106              158400                 15840
Unlisted Equipment                      115385                 11538
General Load                            346153                 34615
--------------------------------------------------------------------------------
TOTAL                                                            230769
==================================================
ANNUAL OPERATING COST - SUMMARY  (2011 prices)
==================================================
Cost Item                          $/Year                      %
--------------------------------------------------------------------------------
Raw Materials                    12401000               67.02
Labor-Dependent                 729000                   3.94
Facility-Dependent               696000                   3.76
Laboratory/QC/QA                109000                   0.59
Waste Treatment/Disposal        4337000               23.44
Utilities                           231000                   1.25
TOTAL                             18503000               100.0
==========================================================
PROFITABILITY ANALYSIS  (2011 prices)
==========================================================
A. DIRECT FIXED CAPITAL                          $               3715000
B. WORKING CAPITAL                                               1609000
C. STARTUP COST                                                   186000
D. UP-FRONT R&D                                                  0
E. UP-FRONT ROYALTIES                                            0
F. TOTAL INVESTMENT (A+B+C+D+E)                         5510000
G. INVESTMENT CHARGED TO THIS PROJECT              5510000
H. REVENUE STREAM FLOWRATES
kg/year of total flow (in S-125)                                 4997520
kg/year of total flow (in S-108)                                   1922249
kg/year of total flow (in S-120)                                     649195
kg/year of total flow (in S-114)                                     420644
kg/year of total flow (in S-110)                                     581981
kg/year of total flow (in S-101)                                   3218560
I. PROCESSING (UNIT) COST
$/kg of S-125                                                        3.702
J. SELLING/PROCESSING PRICE
$/kg of total flow (in  S-125)                                      0.500
$/kg of total flow (in  S-108)                                      0.680
$/kg of total flow (in  S-120)                                      7.200
```

```
$/kg of total flow (in  S-114)                          6.600
$/kg of total flow (in  S-110)                         17.700
$/kg of total flow (in  S-101)                          0.680
K. REVENUES   ($/year)
S-125                                                   2499000
S-108                                                  1307000
S-120                                                  4674000
S-114                                                  2776000
S-110                                                 10301000
S-101                                                 2189000
Total Revenues                                        23746000
L. ANNUAL OPERATING COST                              18503000
M. GROSS PROFIT  (K-L)                                5243000
N. TAXES (40 %)                                       2097000
O. NET PROFIT    (M-N + Depreciation )                3499000
```

APPENDIX B (PROCESS C-C)

```
EXECUTIVE SUMMARY (2011 prices)
 TOTAL CAPITAL INVESTMENT                          2415000  $
 CAPITAL INV. CHARGED TO THIS PROJECT              2415000  $
 OPERATING COST                                     4630000  $/year
 PROCESSING RATE                                    4997520  kg/year of S-125
 UNIT PROCESSING COST                                0.926  $/kg of S-125
 TOTAL REVENUES                                     12707000  $/year
 GROSS MARGIN                                       63.57  %
 RETURN ON INVESTMENT                               208.35  %
 PAYBACK TIME                                       0.97  years
=======================================================
MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2011 prices)
--------------------------------------------------------------------------------
Quantity/                  Description                     Unit Cost     Cost
 Stand-by                                                     ( $ )         ( $ )
--------------------------------------------------------------------------------
   1/0  V-101     Continuously Stirred Reactor              24000          24000
                Volume   = 5689.68 L
                Diameter = 1.43 m
   1/0  V-102     Continuously Stirred Reactor               8000         8000
                Volume   = 786.48 L
                Diameter = 0.74 m
   1/0  PFF-101   Plate & Frame Filter                        36000        36000
                Filter Area  = 6.35 m^2
   1/0  V-103     Continuously Stirred Reactor              7000            7000
                Volume   = 611.31 L
                Diameter = 0.68 m
   1/0  PFF-102   Plate & Frame Filter                        36000         36000
                Filter Area  = 6.49 m^2
   1/0  V-104     Continuously Stirred Reactor           7000               7000
                Volume   = 643.14 L
                Diameter = 0.69 m
   1/0  PFF-103   Plate & Frame Filter                       36000       36000
                Filter Area  = 6.49 m^2
   1/0  V-105     Continuously Stirred Reactor            7000        7000
                Volume   = 581.82 L
                Diameter = 0.67 m
   1/0  PFF-104   Plate & Frame Filter                       35000       35000
                Filter Area  = 6.30 m^2
   1/0  PFF-105   Plate & Frame Filter                       27000       27000
                Filter Area  = 7.13 m^2
   1/0  GR-102    Grinder                                   20000        20000
                Rated Throughput = 631.00 kg/h
                Cost of Unlisted Equipment                61000
TOTAL EQUIPMENT PURCHASE COST                              304000
=======================================================
FIXED CAPITAL ESTIMATE SUMMARY (2011 prices)
A. TOTAL PLANT DIRECT COST (TPDC)                          (physical cost)
=======================================================
  1. Equipment Purchase Cost                          $        304000
  2. Installation                                               179000
  3. Process Piping                                             107000
  4. Instrumentation                                            122000
  5. Insulation                                                   9000
```

```
 6. Electricals                                             30000
 7. Buildings                                              137000
 8. Yard Improvement                                        46000
 9. Auxiliary Facilities                                   122000
                                          TPDC =      1056000
B. TOTAL PLANT INDIRECT COST (TPIC)
 10. Engineering                                           264000
 11. Construction                                          369000
                                          TPIC =           633000
C. TOTAL PLANT COST (TPDC+TPIC)        TPC =         1689000
 12. Contractor's fee                                       84000
 13. Contingency                                           169000
                                        (12+13) =          253000
D. DIRECT FIXED CAPITAL (DFC)     TPC+12+13 =        1942000
=======================================================
RAW MATERIALS COST SUMMARY
=================================================================
 Raw                                    Unit Cost      Annual Amount        Cost
 Material                     ( $/kg )       ( kg )              ( $/yr )          %
-----------------------------------------------------------------------------------------------------
 ion H+                        0.035        653400.00            22869        1.82
 sulfur                        0.000        396000.00              0        0.00
 Sulfuric Acid                 0.070       7999200.00           559944       44.58
 sodium sulphur                0.300       1465200.00           439560       35.00
 Sodium Hydroxid               0.040       5841000.00           233640        18.60
-----------------------------------------------------------------------------------------------------
TOTAL                                     16354800.00          1256000      100.00
=================================================================
WASTE TREATMENT / DISPOSAL (2011 prices) b. LIQUID WASTE
Stream                Unit Cost        Annual Amount                        Cost
 -----------------------------------------------------------------------------------------
 Name                ( $/kg )             ( kg )                       ( $/yr )
S-122              1.000e-001       14904936.44                         1490000
WASTE TREATMENT/DISPOSAL TOTAL COST (b)      1490000
=========================================================
UTILITY REQUIREMENTS (2011 prices) ELECTRICITY
-----------------------------------------------------------------------------------------
Procedure          Equipment                         Annual Amount          Cost
 Name                  Name                             ( kWh )                  ( $/yr )
-----------------------------------------------------------------------------------------
P-1                       V-101                     79200                  15840
 P-2                 V-102                        79200                  15840
 P-3               PFF-101                          198000                  39600
 P-4                 V-103                    79200                  15840
 P-5               PFF-102                        198000                  39600
 P-6                 V-104                        79200                  15840
 P-8             PFF-103                            198000                  39600
 P-9                 V-105                          79200                  15840
 P-10            PFF-104                            198000                  39600
 P-11            PFF-105                            198000                  39600
 P-15            GR-102                             499752                  99950
 Unlisted Equipment                                 117860                  23572
 General Load                                       353578                  70716
TOTAL                                                                      471438
==========================================================
ANNUAL OPERATING COST - SUMMARY  (2011 prices)
==========================================================
Cost Item                         $/Year                    %
 ------------------------------------------------------------------------------------------
Raw Materials                     1256000                27.13
 Labor-Dependent                911000                   19.67
 Facility-Dependent               364000                    7.87
 Laboratory/QC/QA               137000                      2.95
 Waste Treatment/Disposal       1490000                  32.19
 Utilities                          471000                 10.18
TOTAL                             4630000              100.00
=======================================================
PROFITABILITY ANALYSIS  (2011 prices)
=======================================================
A. DIRECT FIXED CAPITAL                           $                1942000
 B. WORKING CAPITAL                                                  375000
 C. STARTUP COST                                                      97000
 D. UP-FRONT R&D                                                   0
 E. UP-FRONT ROYALTIES                                             0
 F. TOTAL INVESTMENT (A+B+C+D+E)                                  2415000
 G. INVESTMENT CHARGED TO THIS PROJECT              2415000
 H. REVENUE STREAM FLOWRATES
```

```
    kg/year of total flow (in S-125)                        4997520
    kg/year of total flow (in S-124)                        2244136
    kg/year of total flow (in S-108)                        2581683
    kg/year of total flow (in S-111)                        443154
    kg/year of total flow (in S-117)                        803193
    kg/year of total flow (in S-121)                        373702
 I. PROCESSING (UNIT) COST
    $/kg of S-125                                            0.926
 J. SELLING/PROCESSING PRICE
    $/kg of total flow (in  S-125)                           0.500
    $/kg of total flow (in  S-124)                           0.340
    $/kg of total flow (in  S-108)                           0.340
    $/kg of total flow (in  S-111)                          12.400
    $/kg of total flow (in  S-117)                           2.150
    $/kg of total flow (in  S-121)                           3.600
 K. REVENUES   ($/year)
    S-125                                                   2499000
    S-124                                                    763000
    S-108                                                    878000
    S-111                                                   5495000
    S-117                                                   1727000
    S-121                                                   1345000
   Total Revenues                                          12707000
 L. ANNUAL OPERATING COST                                   4630000
 M. GROSS PROFIT  (K-L)                                     8077000
 N. TAXES (40 %)                                            3231000
 O. NET PROFIT    (M-N + Depreciation )                 5031000
```

APPENDIX C (PROCESS C-B)

```
 EXECUTIVE SUMMARY (2011 prices)
TOTAL CAPITAL INVESTMENT                                 7194000  $
 CAPITAL INV. CHARGED TO THIS PROJECT                    7194000  $
 OPERATING COST                                         12744000  $/year
 PROCESSING RATE                                         4997520  kg/year of S-121
 UNIT PROCESSING COST                                      2.550  $/kg of S-121
 TOTAL REVENUES                                         13204000  $/year
 GROSS MARGIN                                               3.48  %
 RETURN ON INVESTMENT                                      11.91  %
 PAYBACK TIME                                               8.40  years
=======================================================
 MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2011 prices)
=======================================================
 Quantity/       Description                       Unit Cost         Cost
 Stand-by                                            ( $ )           ( $ )
-------------------------------------------------------------------------------
   1/0  V-101     Continuously Stirred Reactor        30000       30000
                Volume   = 11755.26 L
                Diameter = 1.82 m
   1/0  GR-101    Grinder                              12000       12000
                Rated Throughput = 631.00 kg/h
   1/0  PFF-101   Plate & Frame Filter                29000       29000
                Filter Area  = 10.54 m^2
   1/0  V-102     Continuously Stirred Reactor       37000       37000
                Volume   = 1082.57 L
                Diameter = 0.82 m
   1/0  V-103     Continuously Stirred Reactor        9000        9000
                Volume   = 1004.85 L
                Diameter = 0.80 m
   1/0  V-104     Continuously Stirred Reactor        9000        9000
                Volume   = 1096.54 L
                Diameter = 0.82 m
   1/0  V-105     Continuously Stirred Reactor        9000        9000
                Volume   = 1182.86 L
                Diameter = 0.84 m
   1/0  FSP-101   Flow Splitter                       25000       25000
                Rated Throughput = 57.63 kg/h
   1/0  V-106     Continuously Stirred Reactor        52000       52000
                Volume   = 7523.49 L
                Diameter = 1.56 m
   1/0  EH-101    Electric Heater                    100000      100000
                Power  = 101.56 kW
   1/0  EH-102    Electric Heater                   100000      100000
                Power  = 7.11 kW
   1/0  EH-103    Electric Heater                   100000      100000
```

```
          Power  = 84.25 kW
  1/0  EH-104    Electric Heater                  100000      100000
          Power  = 25.91 kW
  1/0  DE-101    Dead-End Filter                   39000       39000
          Filter Area  = 8.96 m^2
  1/0  DE-102    Dead-End Filter                   40000       40000
          Filter Area  = 10.11 m^2
  1/0  DE-103    Dead-End Filter                   40000       40000
          Filter Area  = 9.70 m^2
  1/0  DE-104    Dead-End Filter                   39000       39000
          Filter Area  = 8.93 m^2
==================================================================
 TOTAL EQUIPMENT PURCHASE COST                           961000
==================================================================
 FIXED CAPITAL ESTIMATE SUMMARY (2011 prices)
==================================================================
 A. TOTAL PLANT DIRECT COST (TPDC)  (physical cost)
  1. Equipment Purchase Cost                  $              961000
  2. Installation                                            553000
  3. Process Piping                                          336000
  4. Instrumentation                                         384000
  5. Insulation                                               29000
  6. Electricals                                              96000
  7. Buildings                                               432000
  8. Yard Improvement                                        144000
  9. Auxiliary Facilities                                    384000
                                              TPDC = 3320000
 B. TOTAL PLANT INDIRECT COST (TPIC)
  10. Engineering                                            830000
  11. Construction                                          1162000
                                             TPIC =    1992000
 C. TOTAL PLANT COST (TPDC+TPIC TPC =     5313000
  12. Contractor's fee                                       266000
  13. Contingency                                            531000
                                         (12+13) =  797000
==================================================================
 D. DIRECT FIXED CAPITAL (DFC)     TPC+12+13 =          6110000
==================================================================
RAW MATERIALS COST SUMMARY
==================================================================
 Raw                     Unit Cost      Annual Amount                   Cost
 Material                 ( $/kg )       ( kg )              ( $/yr )              %
------------------------------------------------------------------------------
 Water                   0.003       18473400.00           55420             2.84
 Vanadium                0.000         138600.00             0               0.00
 Sodium Hydroxid     0.040         9702000.00          388080   19.90
 ion h+                  0.000         514800.00             0               0.00
 sulfur                  0.000         475200.00             0               0.00
 sulphuric acid       0.070       10929600.00          765072   39.24
 sodium sulfate      0.090         554400.00          49896              2.56
 sodium lactate      0.970         712800.00          691416            35.46
------------------------------------------------------------------------------
 TOTAL                                41500800.00        1950000            100.00
==========================================================
 WASTE TREATMENT / DISPOSAL (2011 prices)b. LIQUID WASTE
==========================================================
 Stream                 Unit Cost         Annual Amount            Cost
 Name                   ( $/kg )             ( kg )                   ( $/yr )
-------------------------------------------------------------------------
 S-117               6.000e-002       22696628.83          1362000
 S-134               7.600e-002       16651088.58          1265000
-------------------------------------------------------------------------
WASTE TREATMENT/DISPOSAL TOTAL COST (b)   2627000
=========================================================
 UTILITY REQUIREMENTS (2011 prices) ELECTRICITY
------------------------------------------------------------------------------
 Procedure          Equipment        Annual Amount          Cost
 Name                 Name                ( kWh )               ( $/yr )
------------------------------------------------------------------------------
 leaching           V-101                 55440                5544
 P-2                GR-101               499752              49975
 P-4                PFF-101              118800              11880
 prec. pH 4         V-102                55440                5544
 prec. pH 2         V-103                55440                5544
 prec. pH 3.5       V-104                 55440                5544
 prec pH 6          V-105                55440                5544
 P-8                FSP-101              63360                6336
```

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 P-7              V-106                  55440                5544
 P-10             EH-101               804386               80439
 P-11             EH-102                 56298                 5630
 P-13             EH-103               667268               66727
 P-12             EH-104               205204               20520
 Unlisted Equipment                171732                 17173
 General Load                         515195                 51520
 TOTAL                                                         343463
=====================================================
 ANNUAL OPERATING COST - SUMMARY  (2011 prices)
=====================================================
 Cost Item                          $/Year                   %
------------------------------------------------------------
 Raw Materials                1950000                   15.30
 Labor-Dependent                3643000                   28.59
 Facility-Dependent             1146000                     8.99
 Laboratory/QC/QA                546000                     4.29
 Consumables                     2487000                   19.52
 Waste Treatment/Disposal    2627000                   20.62
 Utilities                           343000                     2.70
 TOTAL                             12744000             100.00
=====================================================
PROFITABILITY ANALYSIS  (2011 prices)
=====================================================
 A. DIRECT FIXED CAPITAL                              $    6110000
 B. WORKING CAPITAL                                          779000
 C. STARTUP COST                                               305000
F. TOTAL INVESTMENT (A+B+C+D+E)                        7194000
 G. INVESTMENT CHARGED TO THIS PROJECT         7194000
 H. REVENUE STREAM FLOWRATES
     kg/year of total flow (in S-121)                         4997520
     kg/year of total flow (in S-129)                           2629970
     kg/year of total flow (in S-131)                         1737159
     kg/year of total flow (in S-132)                           205424
     kg/year of total flow (in S-130)                           525755
     kg/year of total flow (in S-105)                         2055331
 I. PROCESSING (UNIT) COST
     $/kg of S-121                                                        2.550
 J. SELLING/PROCESSING PRICE
     $/kg of total flow (in  S-121)                               0.500
     $/kg of total flow (in  S-129)                               0.690
     $/kg of total flow (in  S-131)                               1.900
     $/kg of total flow (in  S-132)                             18.900
     $/kg of total flow (in  S-130)                               0.550
     $/kg of total flow (in  S-105)                               0.690
 K. REVENUES   ($/year)
     S-121                                                    2499000
     S-129                                                  1815000
     S-131                                                  3301000
     S-132                                                  3883000
     S-130                                                    289000
     S-105                                                  1418000
    Total Revenues                                      13204000
 L. ANNUAL OPERATING COST                         12744000
 M. GROSS PROFIT  (K-L)                                    460000
 N. TAXES (40 %)                                          184000
 O. NET PROFIT    (M-N + Depreciation )                856000
    GROSS MARGIN                                                3.48 %
    RETURN ON INVESTMENT                                  11.91 %
    PAYBACK TIME (years)                                       8.40
```

APPENDIX D (PROCESS B-B)

```
 EXECUTIVE SUMMARY (2011 prices)
=========================================================================
 TOTAL CAPITAL INVESTMENT                          10659000  $
 CAPITAL INV. CHARGED TO THIS PROJECT              10659000  $
 OPERATING COST                                    19652000  $/year
 PROCESSING RATE                                    4997520  kg/year of S-121
 UNIT PROCESSING COST                              3.932  $/kg of S-121
 TOTAL REVENUES                                    27082000  $/year
 GROSS MARGIN                                       27.44  %
 RETURN ON INVESTMENT                               49.71  %
 PAYBACK TIME                                       2.01  years
 ======================================================================
 MAJOR EQUIPMENT SPECIFICATION AND FOB COST (2011 prices)
=======================================================================
 Quantity/       Description                        Unit Cost     Cost
 Stand-by                                              ( $ )      ( $ )
--------------------------------------------------------------------------------
  4/0  V-101     Continuously Stirred Reactor       48000      192000
            Volume   = 38759.66 L
            Diameter = 2.70 m
  1/0  GR-101    Grinder                            12000       12000
            Rated Throughput = 631.00 kg/h
  1/0  PFF-101   Plate & Frame Filter               65000       65000
            Filter Area  = 43.86 m^2
  1/0  V-102     Continuously Stirred Reactor       27000       27000
            Volume   = 3988.59 L
           Diameter = 1.27 m
  1/0  V-103     Continuously Stirred Reactor       27000       27000
            Volume   = 3948.29 L
            Diameter = 1.26 m
  1/0  V-104     Continuously Stirred Reactor       27000       27000
            Volume   = 3968.97 L
            Diameter = 1.26 m
  1/0  V-105     Continuously Stirred Reactor       27000       27000
            Volume   = 3945.44 L
            Diameter = 1.26 m
  1/0  V-107     Continuously Stirred Reactor       52000       52000
            Volume   = 39354.00 L
            Diameter = 2.64 m
  1/0  EH-101    Electric Heater                   100000      100000
            Power  = 58.60 kW
  1/0  EH-102    Electric Heater                   100000      100000
            Power  = 16.77 kW
  1/0  EH-103    Electric Heater                   100000      100000
            Power  = 9.96 kW
  1/0  EH-104    Electric Heater                   100000      100000
            Power  = 40.25 kW
  1/0  DE-101    Dead-End Filter                    61000       61000
            Filter Area  = 35.35 m^2
  1/0  DE-102    Dead-End Filter                    61000       61000
            Filter Area  = 35.49 m^2
  1/0  DE-103    Dead-End Filter                    61000       61000
            Filter Area  = 34.99 m^2
  1/0  FSP-101   Flow Splitter                      25000       25000
            Rated Throughput = 64.21 kg/h
  1/0  DE-104    Dead-End Filter                    61000       61000
            Filter Area  = 35.19 m^2
=======================================================
 TOTAL EQUIPMENT PURCHASE COST                       1370000
=======================================================
 FIXED CAPITAL ESTIMATE SUMMARY (2011 prices)
=======================================================
 A. TOTAL PLANT DIRECT COST (TPDC)               (physical cost)
  1. Equipment Purchase Cost         $            1370000
  2. Installation                                  861000
  3. Process Piping                                480000
  4. Instrumentation                               548000
  5. Insulation                                     41000
  6. Electricals                                   137000
  7. Buildings                                     617000
  8. Yard Improvement                              206000
  9. Auxiliary Facilities                          548000
                                        TPDC =  4808000
 B. TOTAL PLANT INDIRECT COST (TPIC)
  10. Engineering                                 1202000
```

```
 11. Construction                                          1683000
                                              TPIC =     2885000
C. TOTAL PLANT COST (TPDC+TPIC) TPC =     7693000
 12. Contractor's fee                                        385000
 13. Contingency                                             769000
                                       (12+13) =       1154000
==========================================================
 D. DIRECT FIXED CAPITAL (DFC)TPC+12+13 =8847000
==========================================================
RAW MATERIALS COST SUMMARY
=========================================================
 Raw                 Unit Cost      Annual Amount                      Cost
 Material              ( $/kg )        ( kg )                    ( $/yr )    %
-----------------------------------------------------------------------------
 ion h+                 0.001       1100880.00           1101        0.02
 Sodium Hydroxid  0.040       4284720.00          171389       3.81
 Sodium lactate     0.970        926640.00          898841      20.01
 ferric sulfate        0.050      64944000.00        3247200     72.27
 sodium sulfate      0.090        617760.00          55598        1.24
 Water                  0.005     23760000.00         118800       2.64
-----------------------------------------------------------------------------
 TOTAL                            95634000.00        4493000   100.00
=========================================================
 WASTE TREATMENT / DISPOSAL (2011 prices) b. LIQUID WASTE
=========================================================
 Stream                 Unit Cost        Annual Amount          Cost
 Name                  ( $/kg )               ( kg )              ( $/yr )
-------------------------------------------------------------------------
 S-117               1.000e-001       69305069.45          6931000
 S-130               1.000e-001       24796163.75          2480000
========================================================
 WASTE TREATMENT/DISPOSAL TOTAL COST (b)  9410000
========================================================
 UTILITY REQUIREMENTS (2011 prices) ELECTRICITY
-------------------------------------------------------------------------
 Procedure        Equipment             Annual Amount            Cost
 Name              Name                        ( kWh )              ( $/yr )
-------------------------------------------------------------------------
 bioleaching        V-101                  55440                              5544
 P-2              GR-101               499752                              49975
 P-4              PFF-101              118800                              11880
 prec. pH 4        V-102                 55440                              5544
 prec. pH 2        V-103                 55440                              5544
 prec. pH 3.5       V-104                 55440                              5544
 prec pH 6         V-105                 55440                              5544
 P-7              V-107                55440                               5544
 P-9              EH-101               464077                              46408
 P-11              EH-102               132850                              13285
 P-12              EH-103                78895                              7889
 P-13              EH-104               318741                              31874
 P-8              FSP-101               63360                               6336
 Unlisted Equipment                    125570                              12557
 General Load                        376709                              37671
TOTAL                                                                    251139
==========================================================
 ANNUAL OPERATING COST - SUMMARY  (2011 prices)
==========================================================
 Cost Item                       $/Year                          %
---------------------------------------------------------------
 Raw Materials                     4493000                    22.86
 Labor-Dependent                    911000                     4.63
 Facility-Dependent                1658000                     8.44
 Laboratory/QC/QA                 137000                  0.70
 Consumables                     2792000                    14.21
 Waste Treatment/Disposal    9410000                47.88
 Utilities                              251000                  1.28
==========================================================
 TOTAL                          19652000      100.00
=========================================================
 PROFITABILITY ANALYSIS  (2011 prices)
=========================================================
 A. DIRECT FIXED CAPITAL                              $     8847000
 B. WORKING CAPITAL                                        1370000
 C. STARTUP COST                                            442000
 D. UP-FRONT R&D                                                0
 E. UP-FRONT ROYALTIES                                          0
 F. TOTAL INVESTMENT (A+B+C+D+E)                     10659000
```

G. INVESTMENT CHARGED TO THIS PROJECT	10659000
H. REVENUE STREAM FLOWRATES	
kg/year of total flow (in S-121)	4997520
kg/year of total flow (in S-132)	1473264
kg/year of total flow (in S-133)	615772
kg/year of total flow (in S-134)	426250
kg/year of total flow (in S-135)	2264894
kg/year of total flow (in S-105)	1691001
I. PROCESSING (UNIT) COST	
$/kg of S-121	3.932
J. SELLING/PROCESSING PRICE	
$/kg of total flow (in S-121)	0.500
$/kg of total flow (in S-132)	5.360
$/kg of total flow (in S-133)	6.220
$/kg of total flow (in S-134)	25.900
$/kg of total flow (in S-135)	0.690
$/kg of total flow (in S-105)	0.150
K. REVENUES ($/year)	
S-121	2499000
S-132	7897000
S-133	3830000
S-134	11040000
S-135	1563000
S-105	254000
Total Revenues	27082000
L. ANNUAL OPERATING COST	19652000
M. GROSS PROFIT (K-L)	7430000
N. TAXES (40 %)	2972000
O. NET PROFIT (M-N + Depreciation)	5299000
GROSS MARGIN	27.44 %
RETURN ON INVESTMENT	49.71 %
PAYBACK TIME (years)	2.01