

CHAPTER 7– FLOTATION OF SULPHIDE MINERALS

Contents: Xanthate adsorption. Oxidation reactions. Activation & depression. Flotation of chalcopyrite, galena, sphalerite, pyrite. Selective flotation. Pb-Zn bulk flotation.

Sulphide minerals are floated by sulphydryl collectors (thio-compounds)

Adsorption of Sulphydryl Collectors:

Adsorption of sulphydryl collectors may occur mainly by chemisorption at metal ion sites on a surface, and by electrochemical mechanisms. Also physisorption may occur by van der Waals bonding between hydrocarbon chains.

Chemical theory of xanthate adsorption:

Consider first the following reaction:



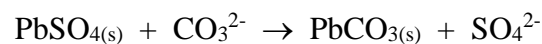
With the following equilibrium expression

$$(a_{\text{PbSO}_4}) / ((a_{\text{PbS}}) \cdot (p_{\text{O}_2})^2) = 10^{124}$$

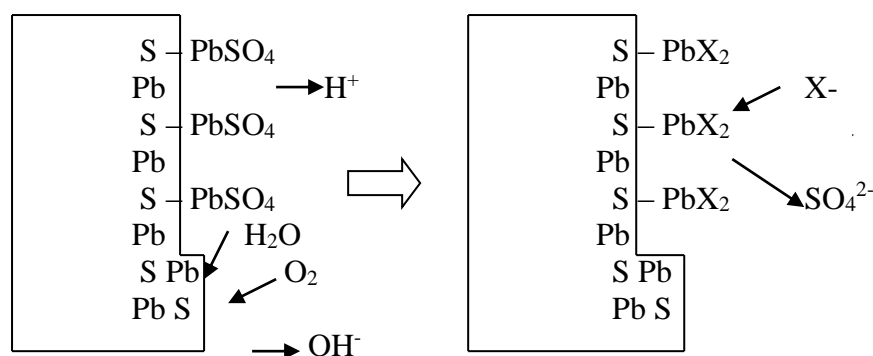
where $a_{\text{PbSO}_4} = 1$
 $a_{\text{PbS}} = 1$
 Therefore $p_{\text{O}_2} = 10^{-62}$ atmosphere

The partial pressure of oxygen in the air is 0.2 atmos. $\gg 10^{-62}$ atmos., thus oxidation of galena occurs to thiosulphate or sulphate.

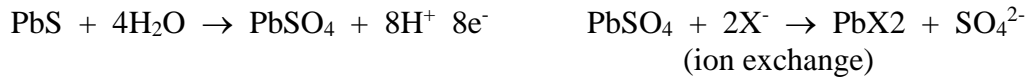
With systems open to air there will also be carbon dioxide present, and the galena surface will form lead carbonate at the expense of sulphate.



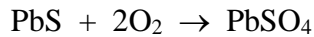
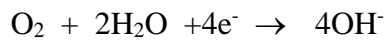
At usual flotation pH of 8 or 9 lead xanthate is more stable than PbCO_3 or PbSO_4 , and PbX_2 forms by replacement of these lead salts.



Anodic:

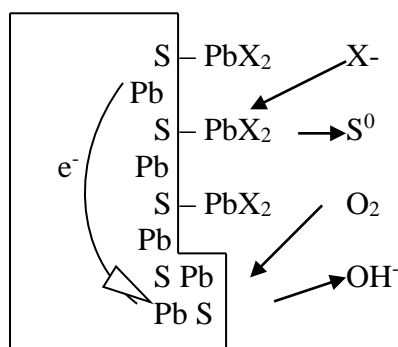


Cathodic:



Electrochemical theory of Xanthate Adsorption

Galena is a semi-conductor which allows electron transfer through the solid. Hence, an electrochemical mechanism has been proposed involving formation of lead xanthate as follows:



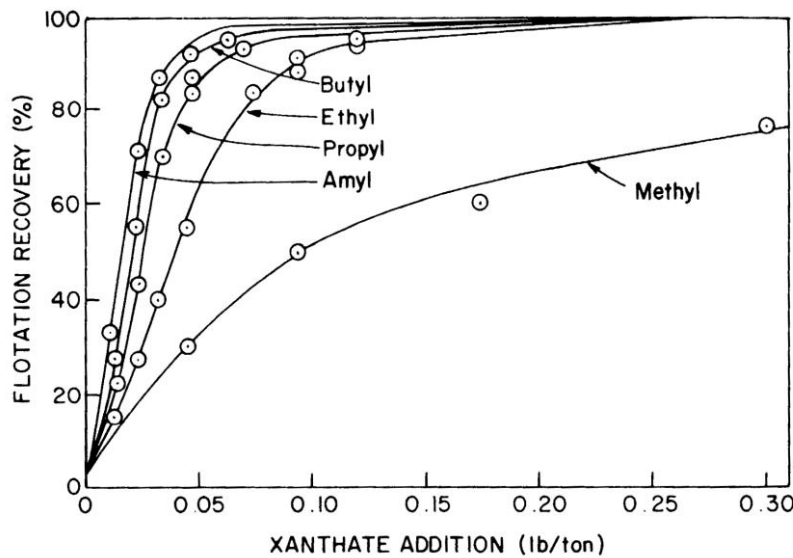
In this model the role of the oxygen is to oxidise lattice sulphide ion to sulphur.

Flotation of Galena (PbS)

Complete flotation of galena is achieved from pH 2 to pH 10 using ethyl xanthate

The collector adsorption mechanisms were discussed above. The hydrophobic metal-collector species responsible for flotation is PbX_2 .

Depending on the hydrocarbon chain length of the collector, the amount of collector required for flotation varies, i.e. the stability of lead xanthates increases as the chain length increases.



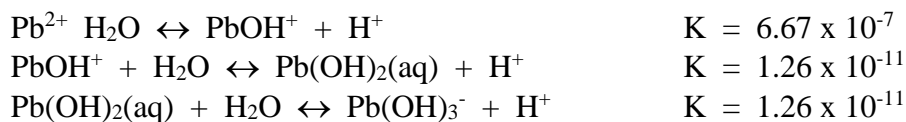
For example, with the same concentration of Pb^{2+} , a smaller concentration of amyl xanthate (C5) is required to form a precipitate of lead amyl xanthate than is required to form lead ethyl xanthate with ethyl xanthate.

The longer the hydrocarbon chain, the greater is the hydrophobicity imparted to the mineral surface.

Depression of Galena:

1. Hydroxyl as depressant (OH^-)

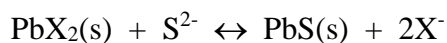
Galena depression at pH values above pH 11 is due to the formation of the lead hydroxy species, plumbite, $Pb(OH)_3^-$, the hydrolysis product of Pb^{2+}



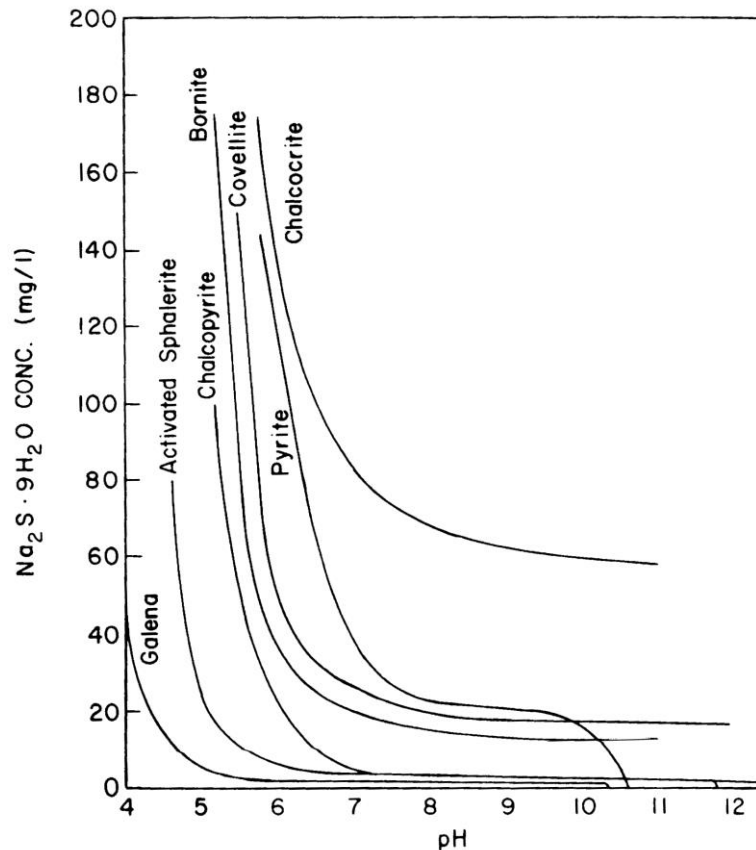
$Pb(OH)_3^-$ forms on the galena surface in preference to lead xanthate.

2. Sulphide as depressant (S^{2-})

Lead sulphide is a very insoluble compound so that additions of sodium sulphide (Na_2S) result in the formation of lead sulphide rather than lead xanthate.



The depression effect of S^{2-} depends on pH of the solution. Of all the sulphides listed, galena exhibits the greatest sensitivity to sulphide ion; it is an effective depressant for galena.



3. Chromate as depressant (CrO_7^{2-})

Lead chromate (PbCrO_7) is a sparingly soluble compound. As a result, when chromate salts are added to a galena system, the formation of lead chromate on the galena surface will occur.

Depression is ascribed to the strong hydration of chromate adsorbed on the surface.

4. Cyanide as a depressant (CN^-)

Cyanide ion does not form a complex with lead ion at moderate concentrations. Hence it does not depress galena.

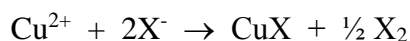
Flotation of Chalcocite (Cu_2S)

Chalcocite (Cu_2S) and chalcopyrite (CuFeS_2) are the two most commonly floated copper sulphide minerals. Bornite (Cu_5FeS_4) and covellite (CuS) and energite (Cu_3AsS_4) are normally present in lesser quantities.

The complete flotation of chalcocite is achieved between $\text{pH} = 1$ to $\text{pH} = 10$ with ethyl xanthate. The resulting hydrophobic species is CuX .

1. Hydroxyl as depressant (OH^-)

Chalcocite is floated at high pH values because of the stability of cuprous (Cu^+) ethyl xanthate relative to cuprous hydroxide. In the xanthate – copper system cuprous xanthate is formed by the following reaction



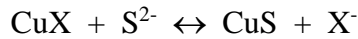
Stability constants for the system are:

Formation of CuX - 5.2×10^{-20}

Formation of Cu(OH)_2 - 2×10^{-15}

2. Sulphide as depressant (S^{2-})

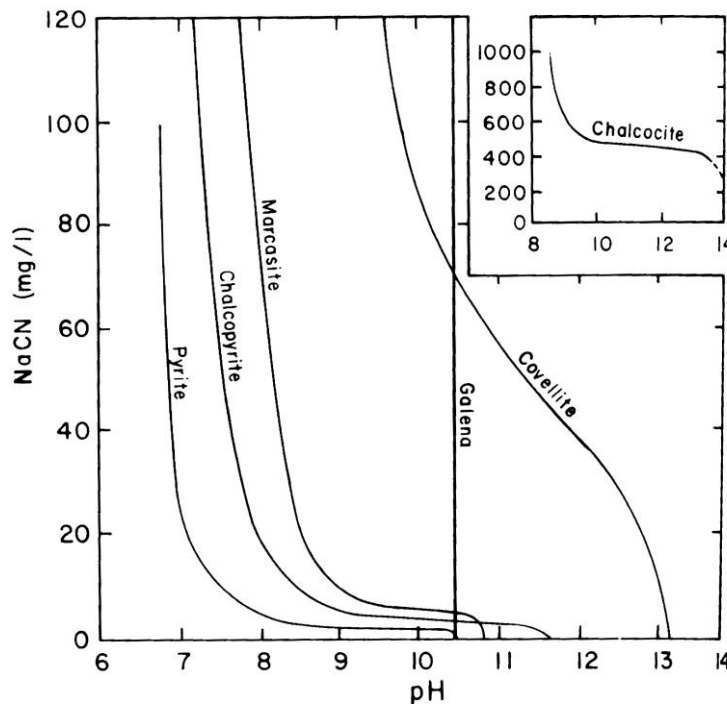
Sulphide should function in a manner similar to galena



CuS is a very insoluble compound and hence it exhibits the least sensitivity to sulphide additions of the minerals examined.

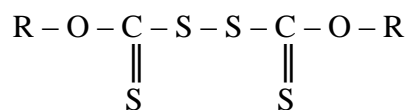
3. Cyanide as depressant (CN^-)

In the presence of cyanide and the absence of iron, chalcocite is depressed only with very high additions of cyanide.

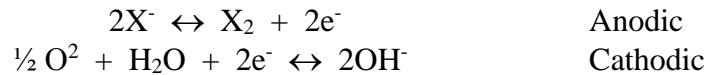


Flotation of Pyrite (FeS_2)

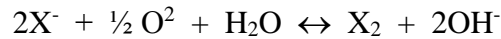
The species of xanthate responsible for the flotation of pyrite in the presence of short chained xanthates is dioxanthogen (X_2) – a dimer of xanthate. Dioxanthogen is an electrically neutral dimer.



Dioxanthogen forms by anodic oxidation of xanthate ion on the surface of the pyrite coupled with cathodic reduction of adsorbed oxygen.



The overall reaction is:



This reaction is possible up to approximately pH 11. Above pH 11 dioxanthogen is not stable with respect to xanthate ion.

Flotation of pyrite is possible below pH 11 with short chain xanthates, but is depressed above about pH 11

Depression of Pyrite

1. Hydroxyl as depressant (OH^-)

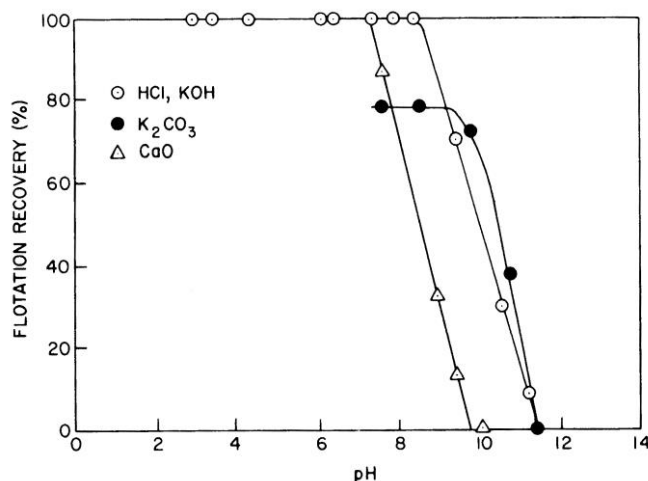
The hydroxyl ion functions as a depressant for two reasons:

- With high hydroxyl activities, above pH 11, xanthate oxidation to dioxanthogen does not occur. The following reaction goes to the left under these conditions



- Above pH 11, the surface of pyrite is of ferric hydroxide ($Fe(OH)_3$), a hydrophilic compound.

Calcium ion contributed by lime in pH adjustment also adds to pyrite depression. Flotation is affected about one pH unit lower if CaO is used for raising pH compared with KOH or K_2CO_3



The pzc for pyrite is at pH = 6.9. Above pH 6.9 the surface of the pyrite is negatively charged and Ca^{2+} adsorbs readily by electrostatic attraction and this hinders the oxidation reaction on the pyrite surface.

2. Cyanide as depressant:

The formation of ferric ferrocyanide on the surface of pyrite is proposed to occur by the following reaction:



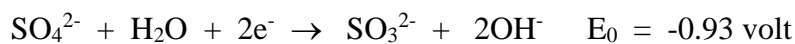
This cyanide complex depresses pyrite from about pH 6 to pH 11. Above pH 11 the stable species on pyrite surface is $\text{Fe}(\text{OH})_3$.

3. Sulphite as depressant (SO_3^{2-})

Since dithionite is the species responsible for pyrite flotation



Reagents that are more reducing than the dithionite- xanthate couple should function as depressants for pyrite. By addition of SO_3^{2-} ions the cell potential can be reduced to lower than $E_0 = -0.06$ volt.



4. Sulphide as depressant (S^{2-})

The half cell of the sulphur-sulphide couple is



This couple is sufficiently reducing for the sulphide ion to function effectively as a depressant for pyrite.

Chemisorption of sulphide ions on pyrite probably occurs similarly to sulphite ion on pyrite.

Flotation of Chalcopyrite (CuFeS_2)

Complete flotation of chalcopyrite is possible from pH 3 to pH 12 with ethyl xanthate.

Both electrochemical oxidation of xanthate to dithionite as well as chemisorption of xanthate on chalcopyrite are responsible for flotation when xanthate is added as collector.

Depression of chalcopyrite

1. Hydroxyl as depressant

CuX is very stable so that hydroxyl ions can only act as a depressant for chalcopyrite at very high values of pH (pH > 13!).

2. Cyanide as depressant

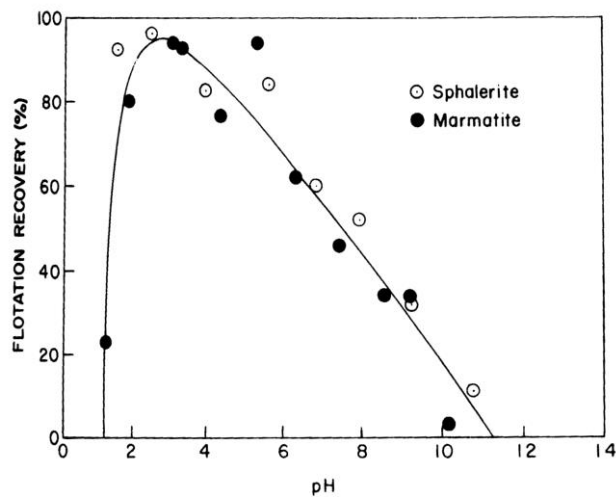
Since both electrochemical oxidation of xanthate to dixanthogen and chemisorption of xanthate are involved in chalcopyrite flotation, it would be expected that chalcopyrite is as sensitive to cyanide additions as pyrite is.

3. Sulphide as depressant

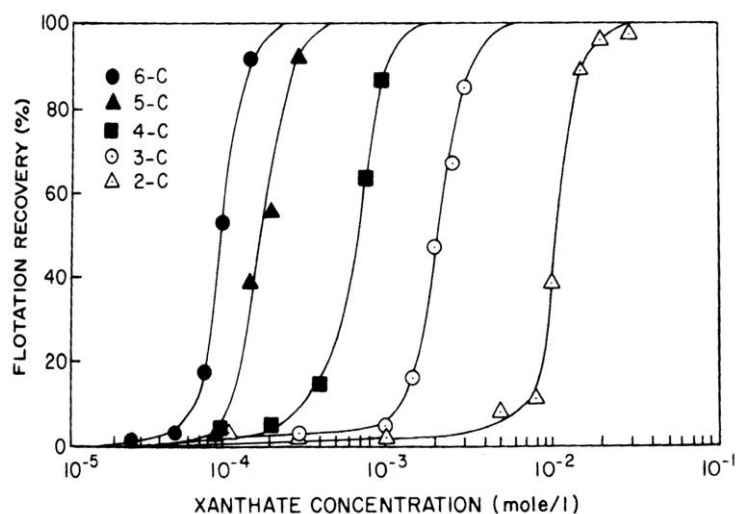
- Very stable cupric sulphide (CuS) will occur due to chemisorption of sulphide ions.
- Oxidation potential of the solution will be lowered when sulphide ion is added. Hence formation of dixanthogen and cuprous xanthate is inhibited.

Flotation of Sphalerite (ZnS)

Flotation of sphalerite with amyl xanthate is possible at pH 3.5 and decreases as the pH is increased.



At higher concentrations of longer chain xanthates sphalerite responds quite readily to flotation



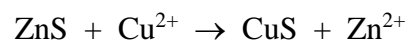
Solubility products of zinc xanthates

Zinc xanthate	Solubility product
Ethyl (C2)	4.9×10^{-9}
Propyl (C3)	3.4×10^{-10}
Butyl (C4)	3.7×10^{-11}
Amyl (C5)	1.55×10^{-12}
Hexyl (C6)	1.25×10^{-13}

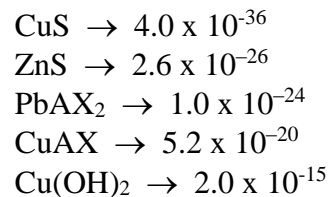
Since the stability of Zn(OH)_2 is greater than zinc-xanthate products it is very difficult to float sphalerite without activation.



Sphalerite is activated with copper sulphate



Forming copper sulphide on the surface. The stability of CuS is greater than ZnS and Zn(OH)_2 .



Thus sphalerite is floated with xanthate after activation with copper.

Prevention of activation

Unintentional activation of sphalerite in ores is most commonly due to Cu^{2+} and Pb^{2+} .

- In the case of Cu^{2+} , cyanide is most commonly used to prevent activation. Cu^{2+} tends to form a complex with cyanide Cu(CN)_2^- .
- In the case of Pb^{2+} , ZnSO_4 is added as a source of Zn^{2+} . When activity of Zn^{2+} is 1000 times greater than Pb^{2+} in solution, the activation by Pb^{2+} will be prevented.

Selective Flotation:

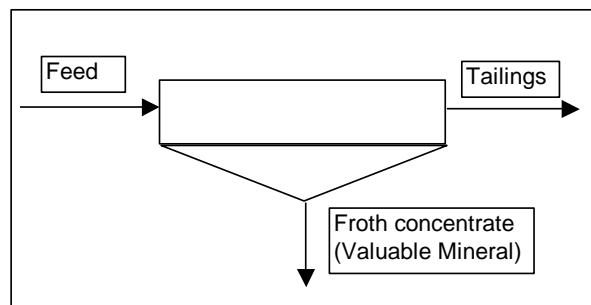
The aim is to remove separate concentrates in a complex ore. This is driven by smelting practice and concentrate contracts which penalise impurities in. For example in a lead/zinc sulphide ore the galena can be floated first at higher pH using cyanide to prevent sphalerite and pyrite from floating. Then activation of sphalerite with copper sulphate and high pH to depress pyrite enables a sphalerite concentrate to be made. Finally a lowering of pH can enable a pyrite concentrate to be made if required.

Bulk Flotation:

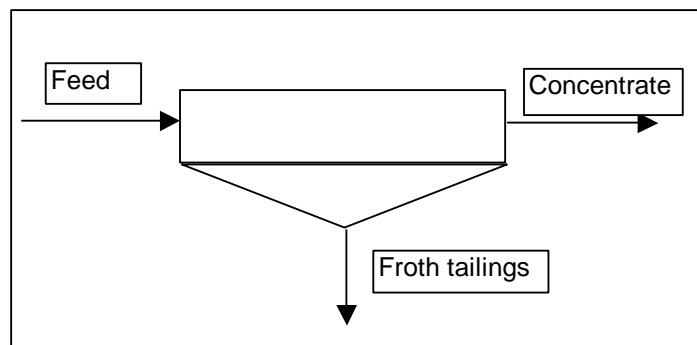
For new smelting practices, eg ISF furnace, and for precious metal recovery in sulphides, it is sometimes preferable to make a bulk concentrate of all sulphides together. In this case no depressants are needed, sphalerite is activated if present, and pH is kept around neutral.

Types of Flotation

Direct Flotation: Valuable minerals are floated into the froth. The sink fraction is the tailings.



Reverse – Indirect – Flotation: Gangue minerals and/or impurities are floated into the froth, and the sink fraction is the concentrate. This technique is widely employed with silicates and oxides flotation, especially in glass sands (quartz), feldspar, kaolin, etc.

**Mode of Flotation**

Selective – Differential – Flotation: Most of the metallic minerals, especially copper, lead, zinc, etc are floated one by one. This is termed selective or differential flotation.

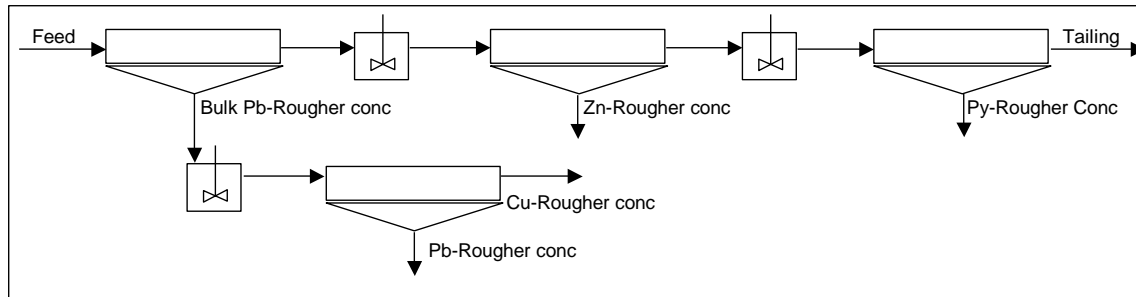
The general sequence for the flotation is as follows:

Lead sulphide (PbS) is floated first. If there is some copper such as chalcopyrite, covellite, etc, that is floated with the lead. Precious metals silver and gold also are collected in this primary concentrate.

After lead or lead and copper flotation, *zinc sulphide* (sphalerite, ZnS) is floated.

Pyrite (FeS) is sometimes floated last.

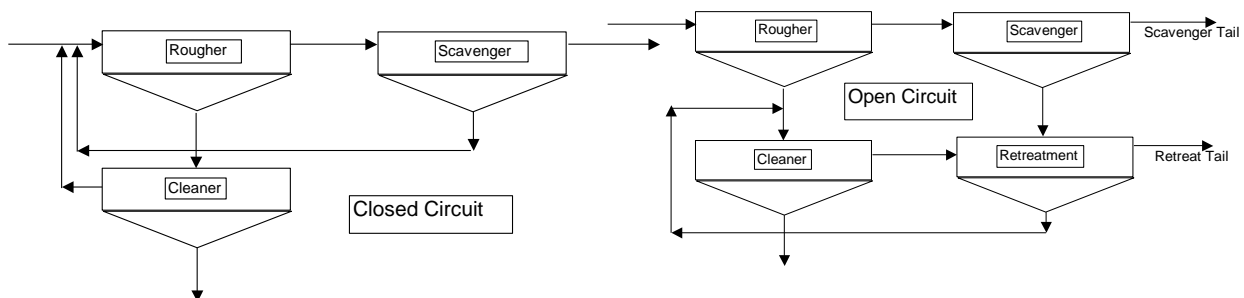
If lead and copper are floated together it is termed a copper-lead bulk rougher concentrate. These can then be separated by floating lead or copper, whichever is the minor component



Bulk Flotation: All valuable minerals (Pb + Zn + Cu + Ag + Au ..) may be floated together into the same mixed *bulk concentrate*. This can be necessary due to the complex nature of the ore or for economic reasons.

- Some Pb-Zn-Ag complex fine grained ores may be floated in this way, while pyrite and gangue are suppressed, for ISF treatment (Imperial Smelting Furnace) which is the only available process for such concentrates
- Some precious metal ores – Au or PGM – have a bulk float of all sulphides, including iron sulphides, as a preconcentration step when the precious metals are associated with the sulphides

Closed Circuit or Open Circuit:



There are many circuits now arranged in an open circuit arrangement as shown above. This has two advantages.

- Stable control of the circuit is much easier since there is no problem of disturbances being fed back to the head of the circuit through the recycles
- The retreatment section can offer modified treatment conditions more appropriate to the middlings particles. Commonly this involves a regrind mill and modified flotation conditions.

Some Tips on Circuit Operation:

- pH is normally regulated in the grinding section, especially in sulphide flotation. This gives longer conditioning time. In many cases depressants are also added just after the

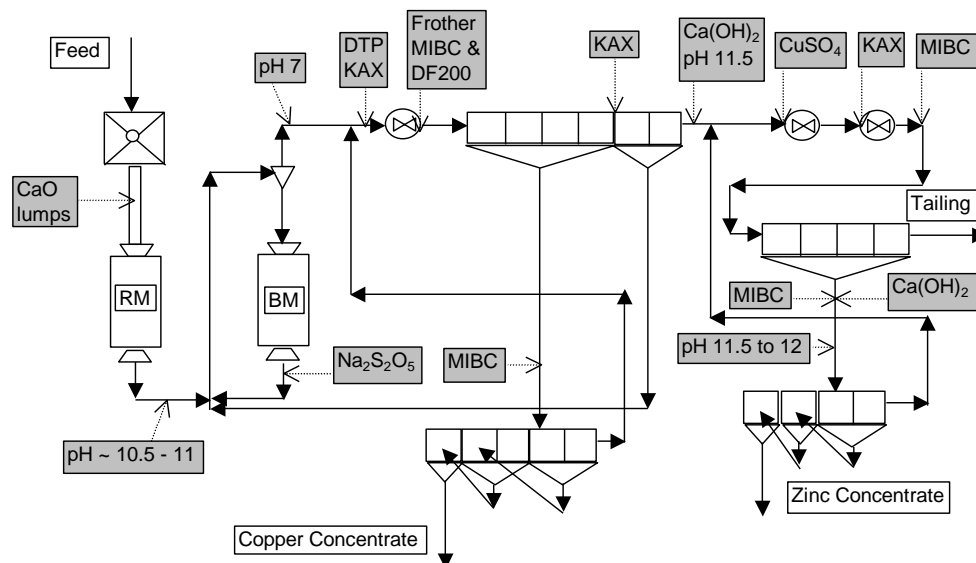
pH regulators during grinding and classification, eg lime to rod mills, cyanides/ $\text{Na}_2\text{S}_2\text{O}_5$ / $\text{K}_2\text{Cr}_2\text{O}_4$ etc to ball mill

- Rougher conditioners are mainly for collector conditioning.
- Pulp density must be regulated before flotation
 - For sulphide flotation

Rougher	30 – 40% wt% solids
Cleaners	15 – 25% wt% solids
 - For non-metallics (oxides/silicates)

Conditioning for fatty acids ~50%, for amines ~ 70% wt% solids

Rougher	30 – 35% wt% solids
Cleaners	20 – 30% wt% solids
- Addition point for chemicals
 - Collectors are normally added at two points.
The major part is always added to the conditioner before rougher flotation
Then a portion is often added at the inlet to the scavengers.
Cleaners normally need no additional collector, but sometimes a little is added at the first cleaning stage
 - Frothers are added to the inlet of the rougher. A further small dosage of frother may be required in the cleaners at the first cleaning stage.
 - Depressants must be added before the collector. In many cases they are added in the grinding section, especially with complex ores.



This example of a mixed sulphide circuit shows a typical arrangement of reagent addition points for the flotation separation.

Sulphide Ores

Since it was first applied industrially, floatation has been applied to sulphide ores of base metals. Some examples are given below. (For more details see Gaudin "Flotation")

▪ Copper Ores

Copper sulphide ores are particularly suitable for flotation.

The ores contain:

- One or more copper sulphides
- Iron sulphides
- Gold and silver
- Quartz, carbonates, silicates

Treatment principles

- Responds well to xanthate at pH 10 – 12
- Pyrite is depressed at high pH

Problems

- Relative abundance of pyrite
- Fine intergrowth with pyrite
- Recovery of precious metals (Au in pyrite)
- Partial oxidation (may require leaching)

▪ **Lead/Zinc Ores**

More challenging to produce selective float and separate minerals

Ores contain

- Galena and sphalerite
- Iron sulphides
- Some copper, gold and silver
- Gangue carbonates, sulphates and silicates

Treatment principles

- Aim for Pb, Cu, Au & Ag in lead concentrate
- Sphalerite only in the zinc concentrate
- Possibly a pyrite con for S &/or Au

Order of flotation generally Pb, Zn, (Py)

- Pb floated with xanthate at pH 8 – 10 using lime or soda ash
- Cyanide or alkali sulphite used to depress the zinc
- Activate sphalerite with CuSO_4 – xanthate at pH 10 – 12
- Flotation of pyrite is comparatively difficult. Drop pH to about 4 to clean the surfaces then float with xanthate about pH 6 – 7

▪ **Copper/Nickel Ores**

Ores contain

- Chalcopyrite
- Pentlandite (NiFeS_2) and pyrrhotite
- Ferromanganese silicates

Order of Flotation

- Bulk copper-nickel concentrate

- Scavenger nickel-iron concentrate
- The bulk concentrate is separated into a copper concentrate and a nickel concentrate which joins the scavenger concentrate as smelter feed
- Flotation used again in *the nickel smelter*. After controlled cooling and grinding of the copper-nickel matte a copper flotation concentrate is sent to copper smelter

▪ ***Copper/Molybdenum Ores***

Ores contain

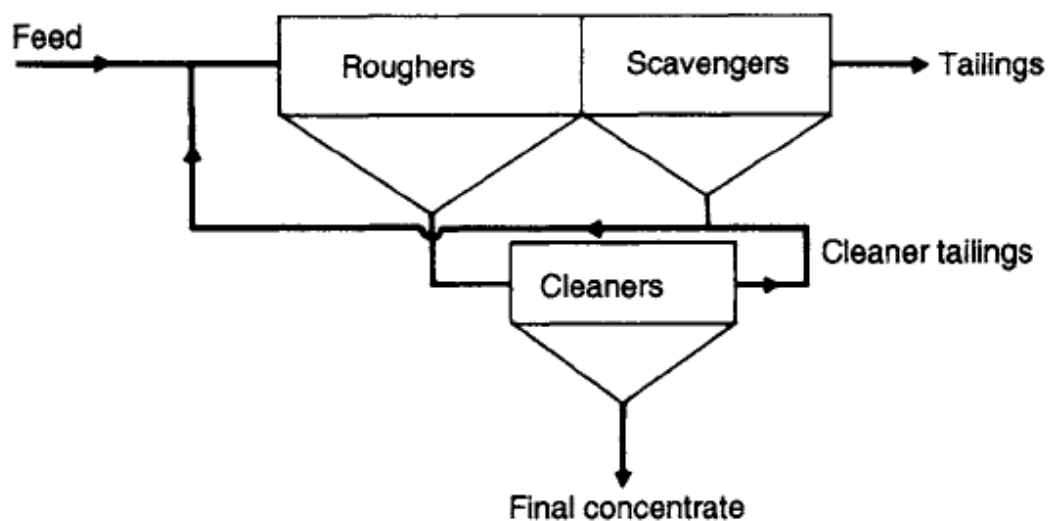
- Molybdenite is found as a minor constituent in some disseminated copper ores

Treatment order

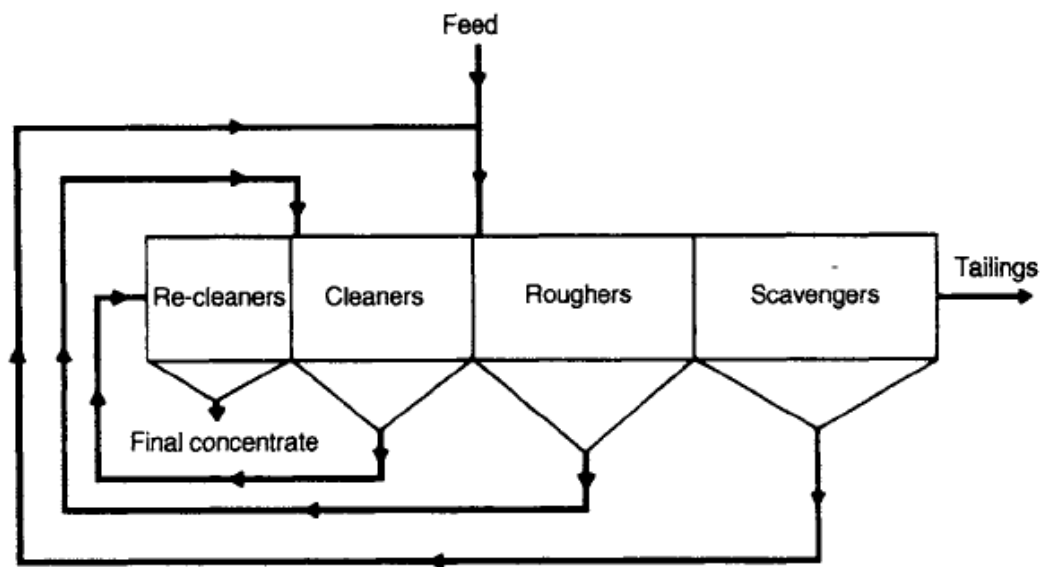
- Molybdenite floated with the copper in a bulk float
- Copper collector destroyed and molybdenite then floated with hydrocarbon collector in a reverse flotation to leave a copper tail.

EXAMPLES OF FLOWSHEETS FOR SULPHIDE FLOTATION CIRCUITS

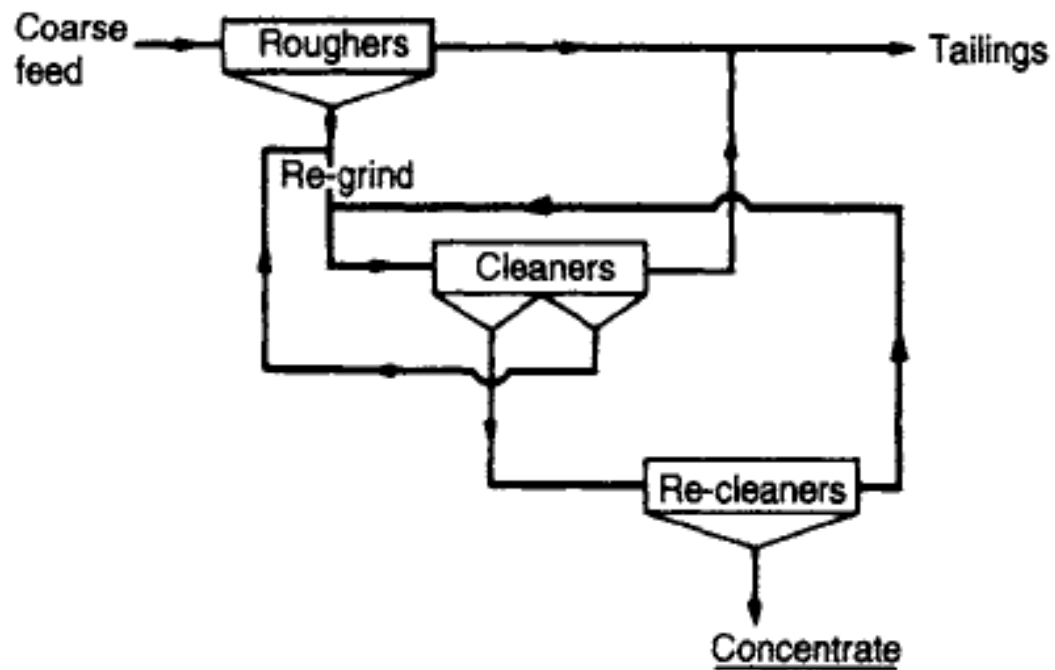
A Simple Rougher-Scavenger and Cleaner Circuit



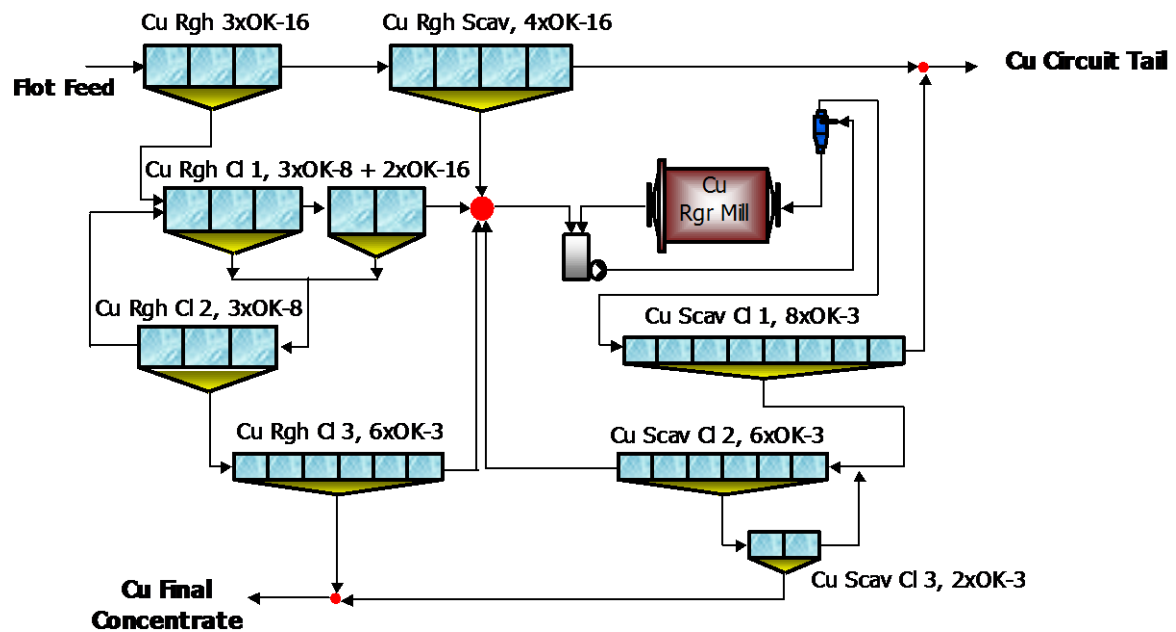
Flotation Circuit with more than one cleaning stage:



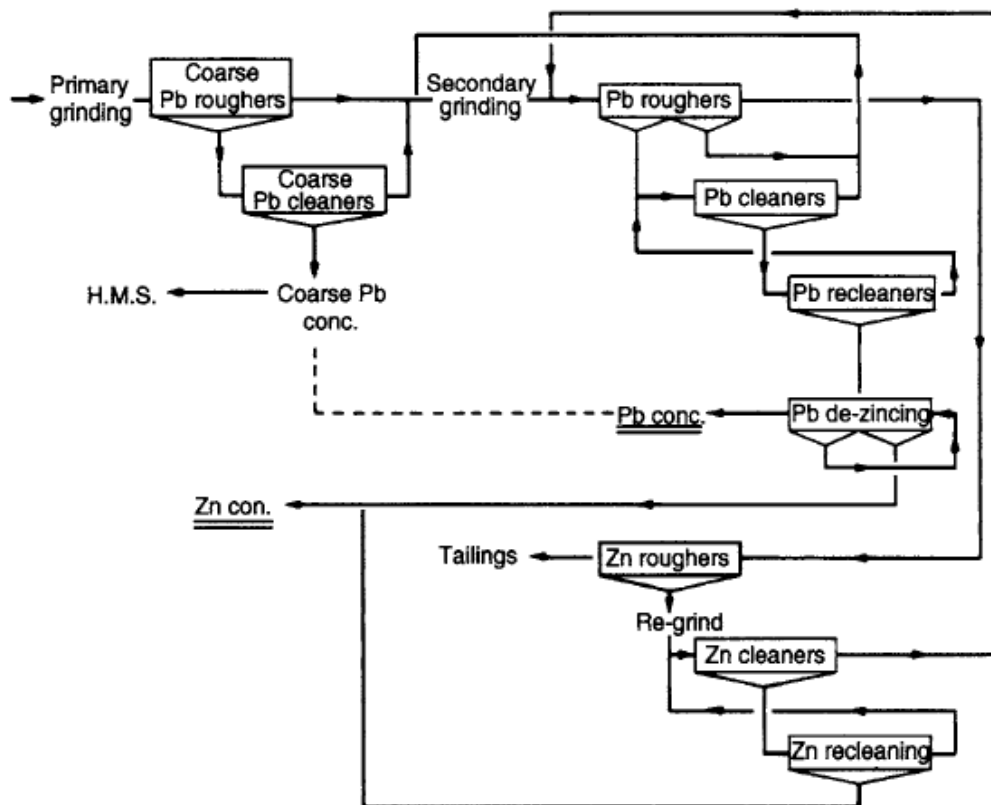
An example of Regrinding of Rougher Concentrate

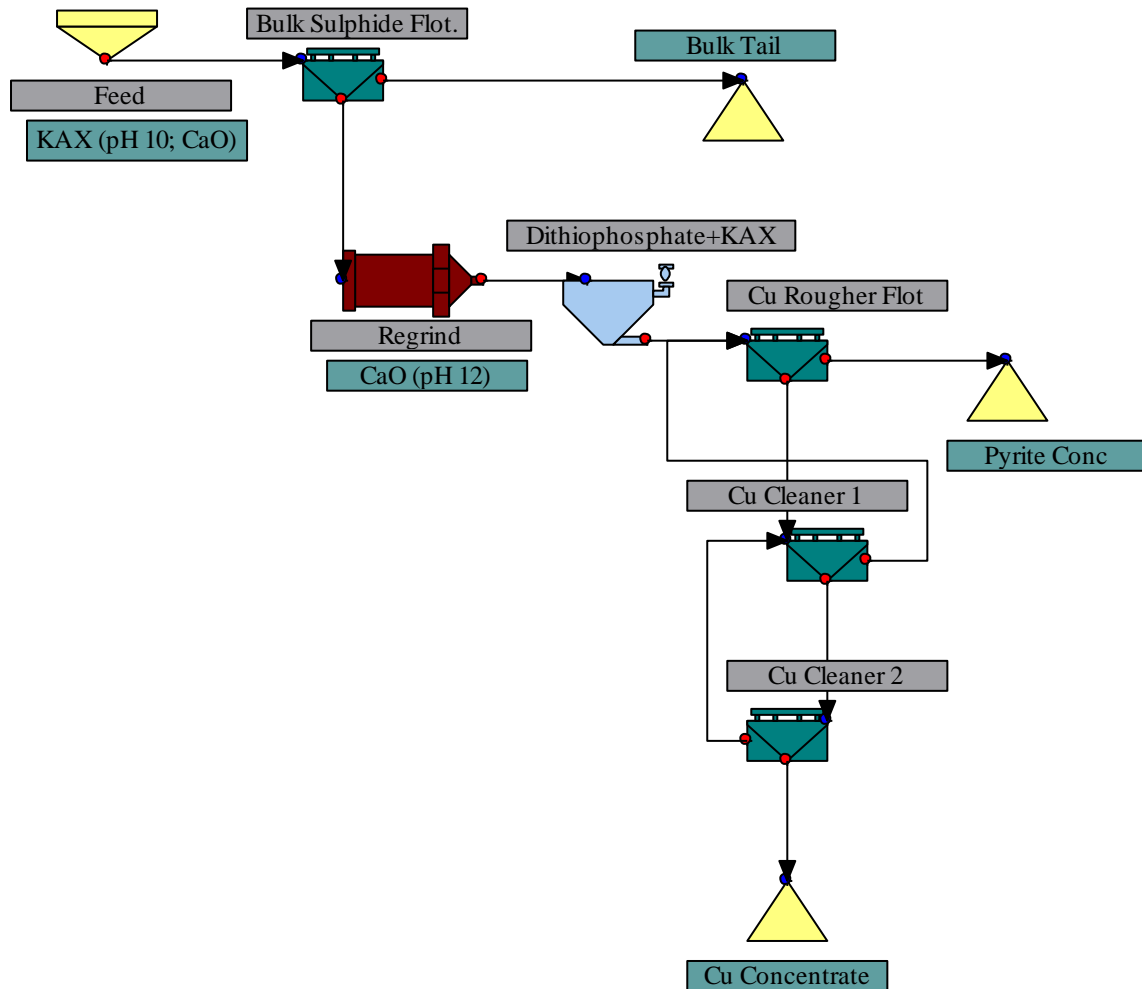


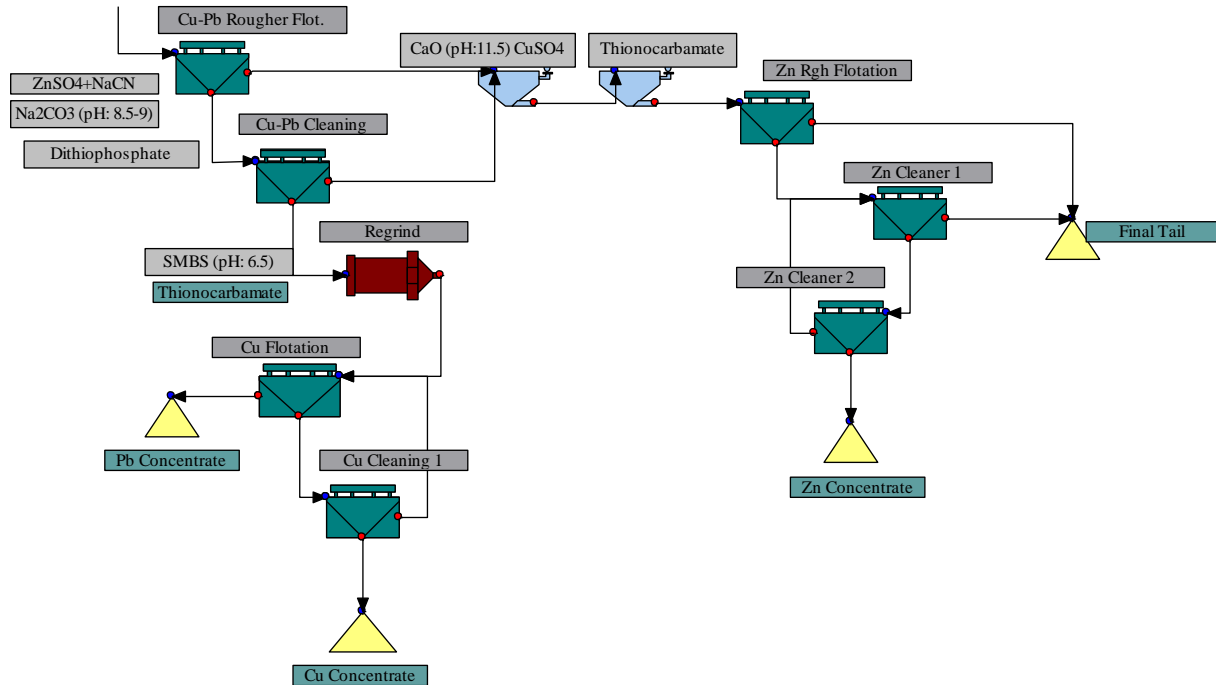
Flowsheet of the Copper Circuit of a Complex Sulphide Ore Flotation Plant



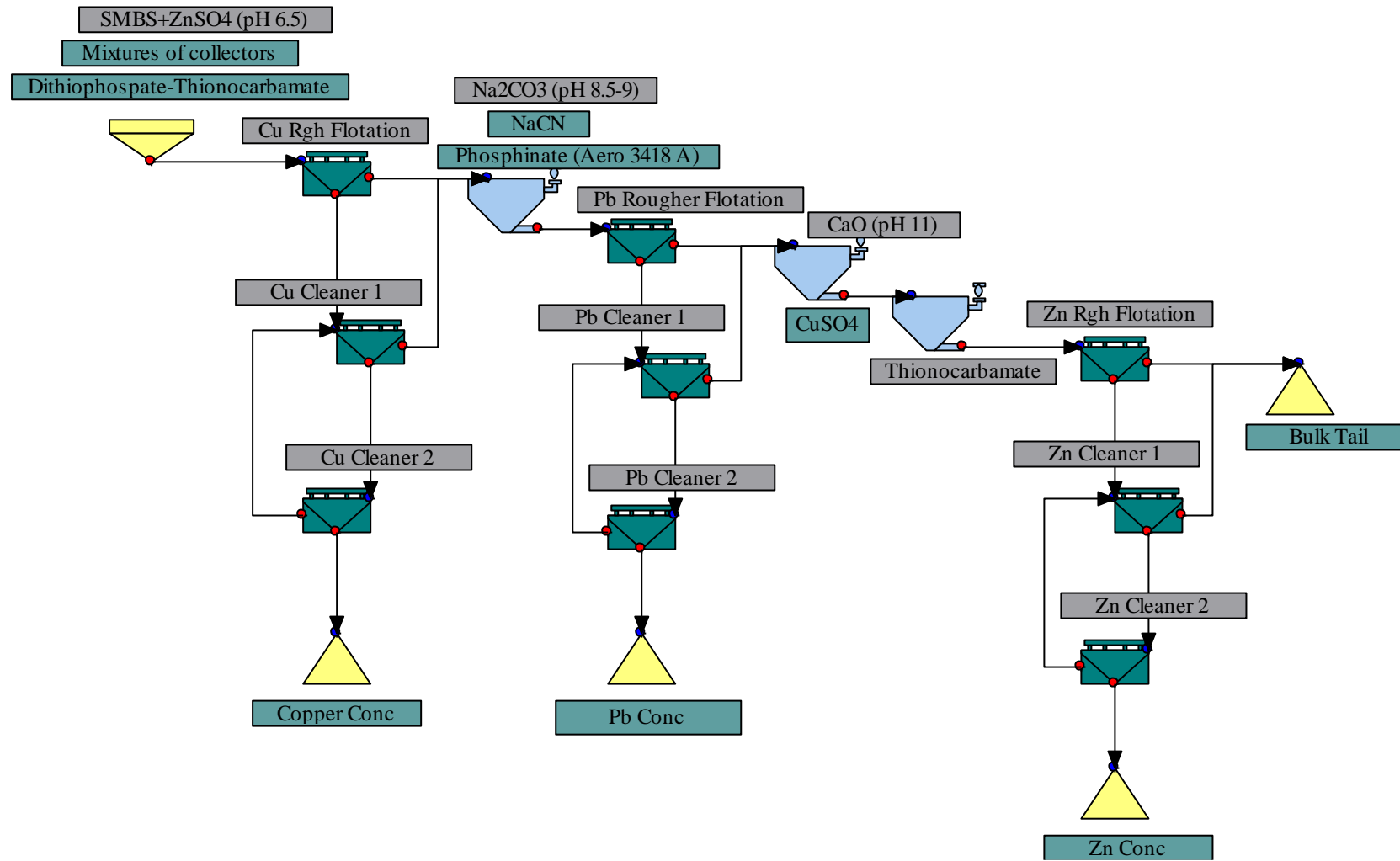
A Flowsheet for Pb-Zn Sulphide Flotation



An example of Bulk Flotation and Porphyry Copper Ore Flotation Circuit

An example of Complex Cu-Zn_Pb Sulphide Ore Flotation Flowsheet

An example of Differential Flotation of Copper-Zinc-Lead Sulphide Flotation Circuits



An example of Chalcopyrite_Pyrite Flotation Circuit

