Chapter 8_Flotation of Non-Sulphide Minerals

Contents: Oxides & silicates. Adsorption & chemisorption of collectors. Activation & depression. Silica, feldspar, calcite, phosphates.

Flotation of Insoluble Oxides and Silicates:

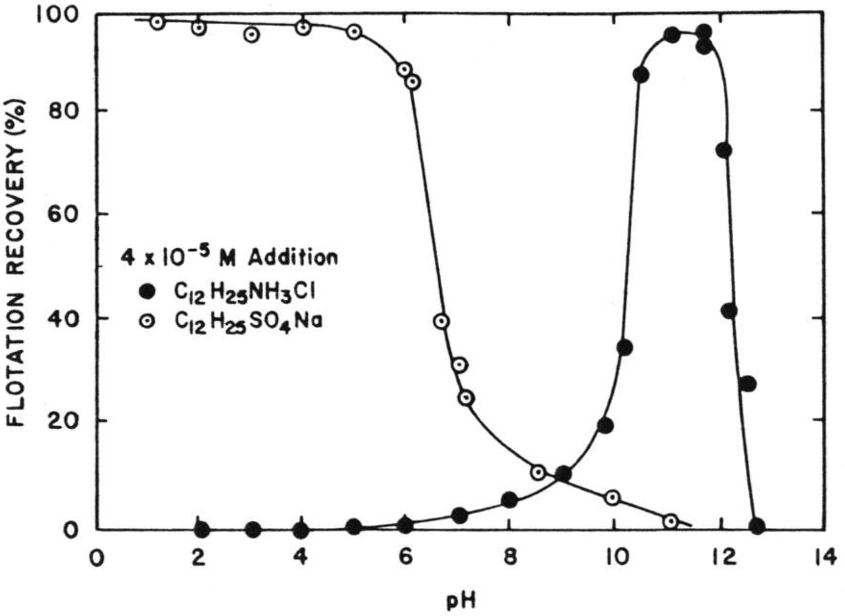
There is a very large number of minerals of this type. Whether or not they float depends on

- Electrical properties of the mineral surface
- Charge of the collector
- Molecular weight of the collector
- Solubility of the mineral
- Stability of the collector/metal salt

Depending on these properties the adsorption may be electrostatic (physical adsorption) or chemical (chemical adsorption)

Flotation by Physical Adsorption

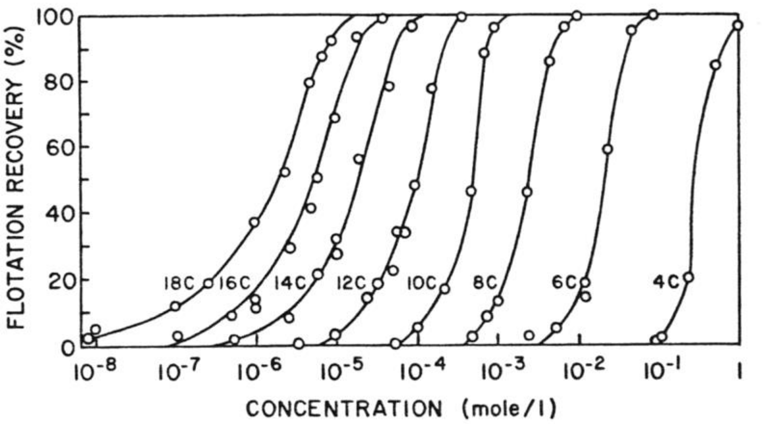
This is common with oxides and silicates. Controlled by the zpc, collector charge and pH. Haematite, alumina and silica have been closely studied. The behaviour of *haematite* (see Lecture 2) and *corundum* (Al_2O_3), below, show this behaviour clearly. The pzc of corundum is 9.1.



Flotation recovery of corundum (Al_2O_3) with $4x10^{-5}$M additions of collector

Quartz has a pzc of 1.8. Anionic collectors such as sulphonates or alkyl sulphates are not adsorbed in sufficient amount below the pzc to promote flotation. This is because anions used for pH adjustment are already present at ionic concentrations greater than 10^{-2} mole/l. The collector must compete with these ions. Above the pzc cationic collectors can be used to float quartz.

Extensive hydrogen bonding of water molecules occurs on oxide and silicate surfaces (ie they are very hydrophilic). As a result long chain collectors (more hydrophobic in character) are very much more effective than short chains. The same flotation result can be achieved with about 10^{-6} as much collector when changing from C4 to C18.



Flotation of quartz in aminium acetate solutions at neutral pH

Modulation of flotation

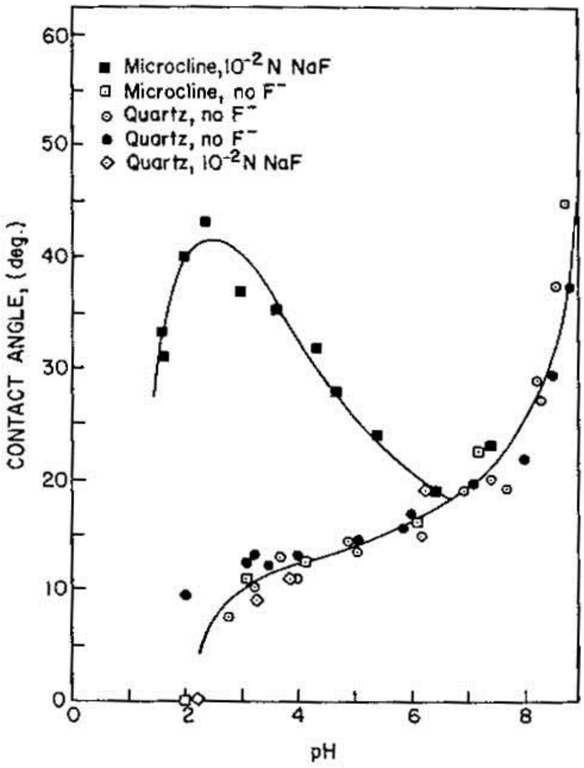
Effect of basicity – the amines are weak bases so that the species present in solution are sensitive to pH. At high pH (pH > 10)

$$RNH_3^+ + OH^- \rightarrow RNH_2 + H_2O$$

The amine species is nolonger charged so the collector is not absorbed and not effective

Activation by fluoride – some silicates are activated by the presence of fluoride. Minerals from the silicate groups were floated as follows:

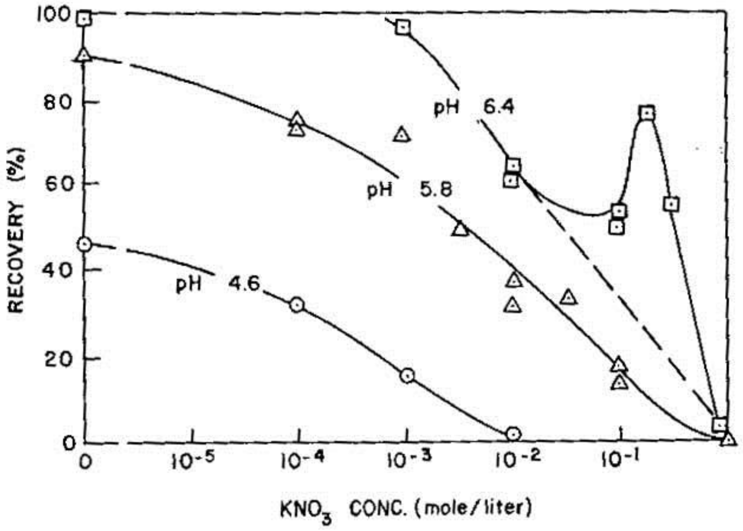
Orthosilicates – eg andalusite, beryl, tourmaline	Sensitive to fluoride
Pyroxenes – eg augite, diopsite, spodumene	Not affected
Amphiboles – eg hornblende, tremolite, actinolite	Not affected
Sheet silicates – eg muscovite, biotite, chlorite	Sensitive to fluoride
Framework silicates – eg quartz, feldspar, nepheline	Less sensitive Quartz not affected



Contact angle of feldspar (microcline) and quartz showing effect of fluoride

Activation is probably by HF attack on surface to give $AlSiF_6^-$ sites for anionic collectors.

Depression with inorganic ions – the inorganic cations compete with RNH_3^+ for surface sites. The effect of potassium nitrate on quartz flotation by dodecylamine at different pHs is shown below. As pH is reduced the surface charge is reduced and the amount of potassium ion needed for depression is also reduced.

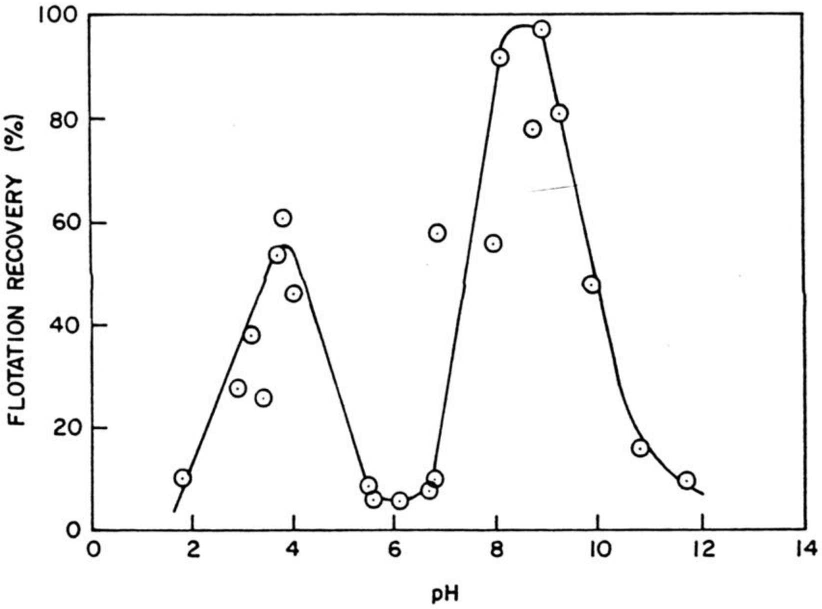


Flotation of quartz showing depression by inorganic ions

Flotation by Chemisorption

Chemisorption of high mlecular weight collectors on oxides and silicates seems to involve the hydrolysis of cations comprising the minerals. The hydroxycomplexes formed are very surface active and adsorb strongly on the solid surfaces.

When pyrolusite (MnO_2) is floated with oleate as collector two maxima are seen in the flotation response. The pzc for this mineral is 7.4.

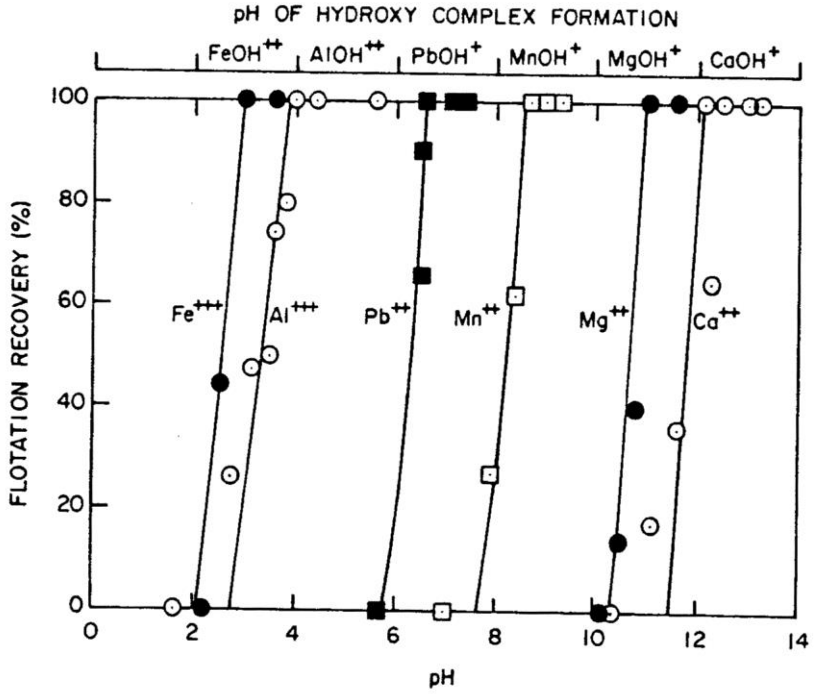


Flotation of pyrolusite (MnO_2) with $1x10^{-4}$M acetate

The strong flotation response at pH 8.5 when the surface is negatively charged cannot be explained by physical adsorption of an anionic collector. It is thought to be due to formation of a hydroxy complex of the manganous ion $MnOH^+$.

The flotation response at lower pH is probably due to physical adsorption of an oleate species.

Activation of quartz by metal ions is a further example of hydroxy-complex formation. The solubility of quartz is very limited and the only cation from the mineral is silicon. Thus quartz activation for flotation by anionic collectors requires metal ions in the pH ranges in which they form hydroxy complexes. For quartz flotation with sulphonate minimum pHs at which flotation occurs are shown below and compared with the pHs of hydroxy complex formation. The pH range for flotation is attributed to the range overwhich sufficient hydroxy complex is present in the system.

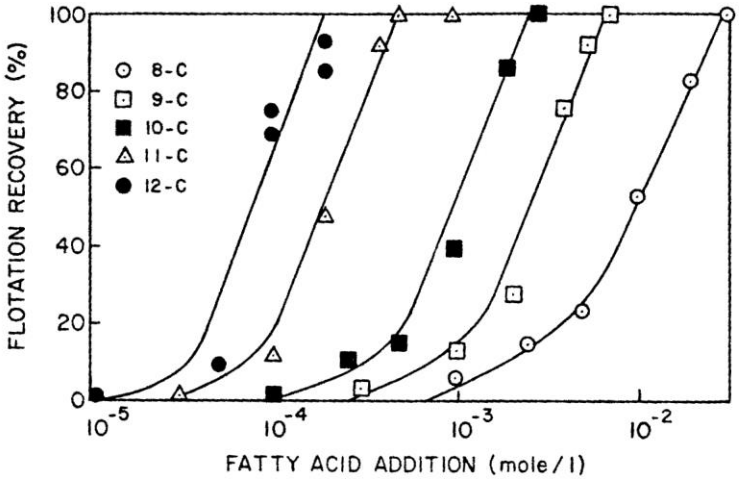


Minimum pH for flotation of quartz with 1x10^{-4}M sulphonate and 1x10^{-4}M metal ion

Semisoluble Salt Flotation:

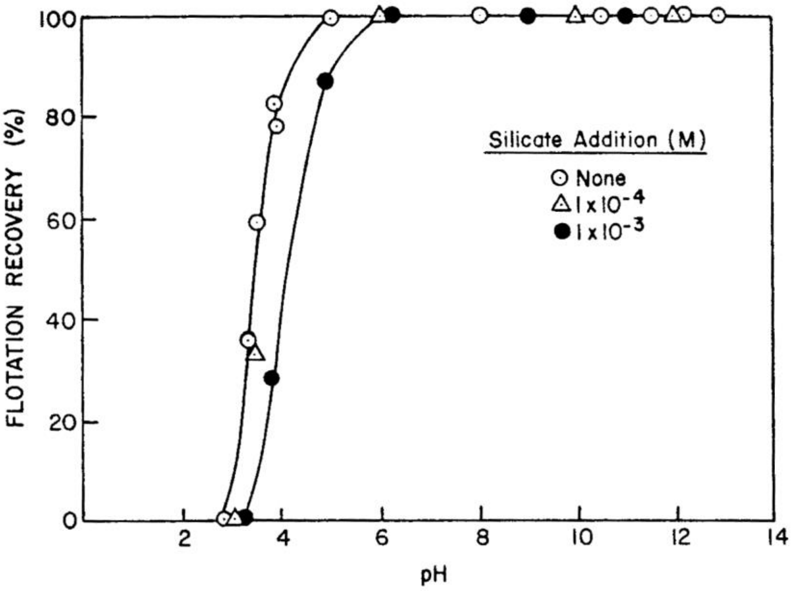
These materials include carbonate, phosphate, sulphate tungstate and some halide minerals. They are characterised by ionic bonding and moderate solubility in water.

Calcite ($CaCO_3$) is a very common mineral in ores. Oleate, and also shorter chain carboxylates, are found to chemisorb on the mineral. There is a strong effect of chain length with flotation occuring at much lower concentrations of collectors when the chain length is increased.



Flotation of calcite at ph 9.7

Apaptite (calcium phosphate) is one of the major non-metallic minerals produced by flotation. The pzc is 6.4 yet as shown below the flotation response with oleate extends well below this pH indicating chemisorption.



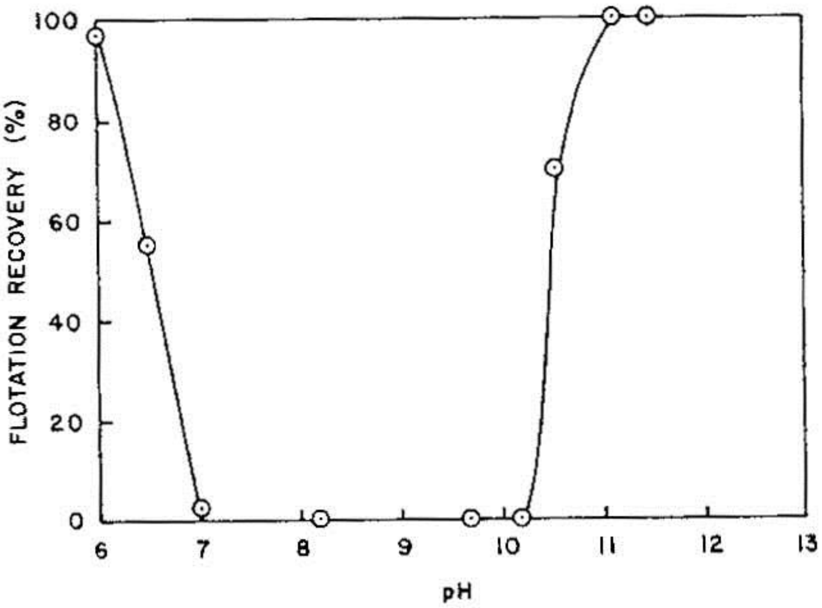
Flotation of apatite with 1×10^{-4}M oleate with and without silicate addition

Rock phosphate contains phosphate as both apaptite and collophane – chemically similar, but porous nodules. Flotation of phosphate to reject quartz requires conditioning at high pulp density with fuel oil. The oil appears to fill the voids in the collophane and to bridge between adsorbed collector molecules.

Depressants for semisoluble salts:

Sodium carbonate. Surface cabonation is an important reaction caused by CO_3^{2-} in solution from CO_2 in the air or carbonate in the ore, eg fluorite (CaF_2) surface is readily given a carbonate coating. There is a practical implication since soda ash is sometimes used for pH control.

Sodium silicate. The composition of aqueous sodium silicates is represented by $mNa_2O.nSiO_2$ where the ratio n/m is te called the modulus and ranges from about 1.6 to 3.8. Some polymerisation of the species occurs to give medium molecular weight units that adsorb as a function of pH and can compete with anionic collectors. They are very effective with calcite over the pH range 7 –10.



Flotation of calcite with $5x10^{-4}$ oleate and $5x10^{-4}$ sodium silicate

With fluorite and apatite there is a minor effect, but with scheelite very little effect. The effect with phosphate is shown above for the flotation of phosphate.

Starches, etc. These natural products are used widely in industry as depressants. Their adsorption properties are strongly effected by molecular weight. They give hydrophillic character to the surface. The problem is selectivity as they tend to adsorb on all surfaces.

Non-Sulphide Ores

A great variety and number of minerals is in this group, including oxides, hydroxides, carbonates, phosphates, sulphates, silicates, tungstates, chromates, molybdenates and manganates. There are the same general problems as with the selective flotation of sulphide minerals – ie separation between different minerals of the same broad class.

In general they can all be floated with carboxylic acids provided there is the correct:

- Collector chain length
- pH
- reagent concentration
- activation where needed

Some may be floated by cationic collectors and some in the Cu/Pb/Zn group by sulfhydryl collectors. Selective flotation needs very careful control of conditions.

Some examples are given below. (For more details see Gaudin “Flotation”)

- **Cu/Pb/Zn oxidised ores**

Ores contain

- Oxides, carbonates and even sulphates

Treatment Problems

- Associated with the gangue minerals
- Oxidised and partially oxidised copper ores generally leached

Treatment approaches by flotation

- Sulphidisation then treat as a sulphide ore
- Use carboxylic acid as collector with gangue depressants
- Using sulfhydryl collectors float base metal minerals from the gangue
- Use long chain primary amines and alkali sulfides for activation

- **Phosphate Ores**

Very large tonnages are floated for the fertiliser industry

Ores contain

- Only members of the apatite series are of commercial significance

Treatment Options

- Anionic collector such as fatty acid used in slightly alkaline pulp to collect phosphate - OR
- Cationic collector such as long chain amine used to float silica at neutral pH

- ***Iron Minerals***

Ores contain

- Haematite, magnetite, goethite and siderite
- Gangue minerals predominately silicates

Treatment Options

- Float iron oxides out of silicates using an anionic collector - OR
- Silica and silicates floated using carboxylic collector at high ph (~11) - OR
- Quartz and silicates floated using cationic collector depressing iron minerals with gums, starches, etc – OR
- Combinations of the above basic approaches

- ***Cassiterite***

Almost the only source of tin, but most is recovered by gravity. Flotation process interesting as with sulphide ores it can include a sulphide flotation also to remove unwanted sulphide.

Treatment process at Renison

- Crush and reject light fraction in heavy medium plant
- Grind and float sulphides to reject heavy minerals
- Gravity separation of cassiterite (very high density)
- Fines to cassiterite flotation – p-tolyl arsonic acid at pH 5 – 6

- ***Quartz***

Very widely present in ores. Very often the aim is to prevent it from floating rather than recovering it by flotation.

Flotation options

- Pure quartz does not float with anionic collectors. Activation with cations is needed to promote flotation. This activation often occurs in complex ores where other cations are present.
- Flotation by amines occurs readily at slightly alkaline pH (8 – 10)

- ***Feldspars***

These are framework silicates, like quartz. They are desireable ceramic raw materials and separation from quartz and mica is important.

Flotation Method

- Feldspar responds like quartz to anionic collectors so not suitable for separation
- Activation with fluoride allows flotation separation from quartz by amines at high pH(~2) (see Lecture 6)

- ***Mica***

Most interest is in K & Li micas (muscovite and lepidolite).

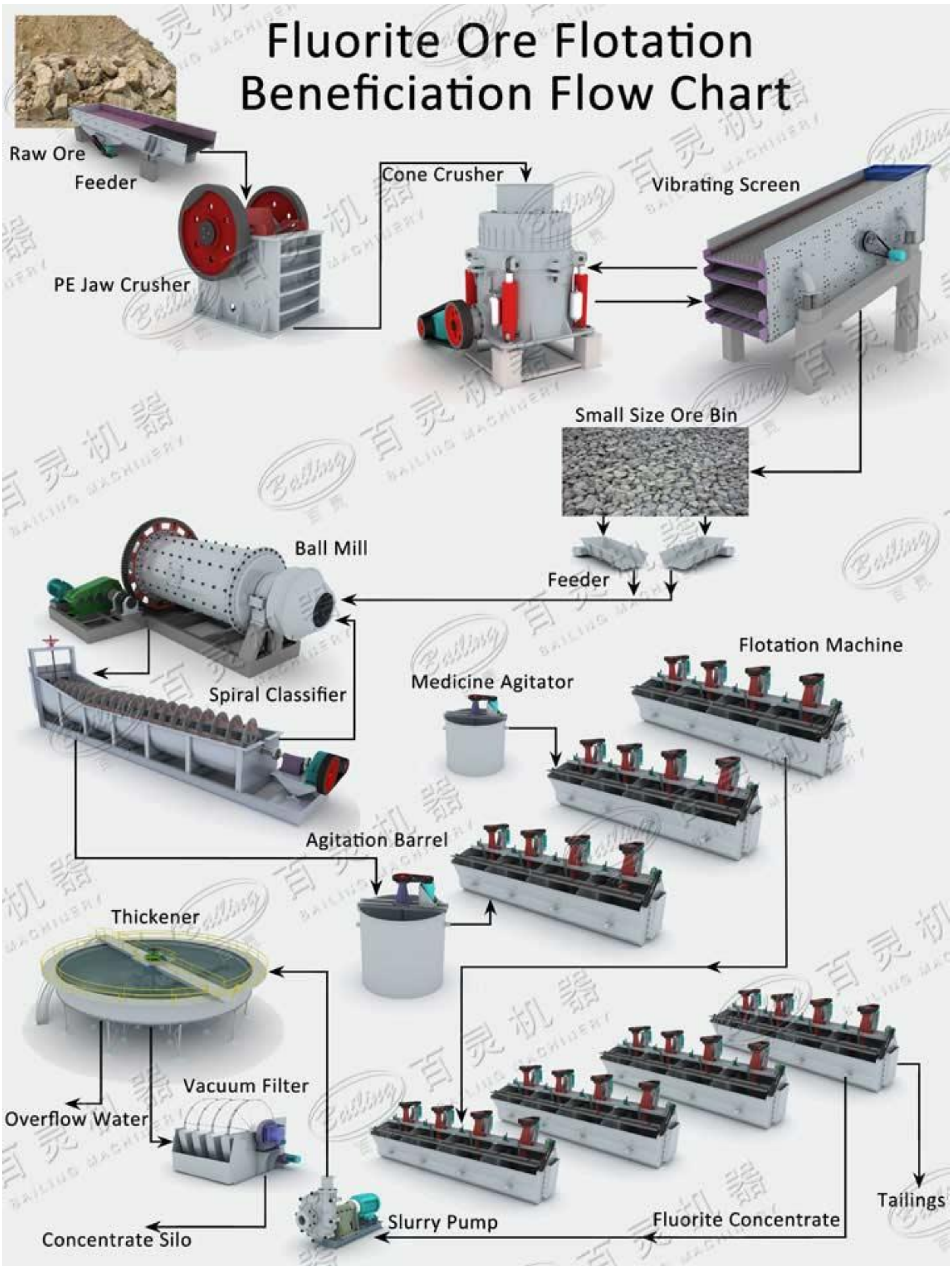
Flotation Method

  - Can be floated with anionic collectors, probably due to activation
  - But generally best recovered by amines in acid solution with added aluminium, probably to depress feldspar

- ***Talc***

Self floating – only a frother is needed. Water glass, soda ash or Calgon used to improve grade of the concentrate.

Often a problem since it floats when it is not wanted and is common in ores.


Fluorite Ore Flotation Beneficiation Flow Chart
Raw Ore
Feeder
PE Jaw Crusher
Cone Crusher
Vibrating Screen
Small Size Ore Bin
Feeder
Ball Mill
Spiral Classifier
Medicine Agitator
Flotation Machine
Agitation Barrel
Thickener
Overflow Water
Vacuum Filter
Concentrate Silo
Slurry Pump
Fluorite Concentrate
Tailings

An Example of Feldspar, Mica and Quartz Flotation Flowsheet , Spruce Pine, North America