Fluxes And Other Materials?

By Rob Boyko

The other day I watched a video of a couple of gents trying to smelter some gold ore using the firing or dry method of assay. There was some confusion as to which fluxes to conjure up and some mistakes were created in their processes. Through trial and error they eventually got it somewhat right. That prompted me to write this article. First let me state that I am not a Chemist nor am I an Assayer. However I do some of my own assay type work in my home lab at times. Many thanks to those who have helped and guided me through time and the knowledge that they have imparted to me; not to mention all those books that I dive into once and a while when I need some insight to a specific problem. Always take caution in any type of assay procedure as some can be devastating to say the least (it can and has been a dangerous process at times). There, that's it, my disclaimer. Once again if you find something in this article that may not be quite right, please contact me and start a conversation. I will respond back, as I too am still learning. So let's get started.

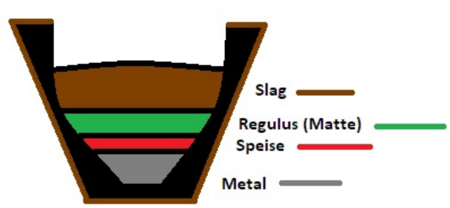
As already aware, the determination of those precious metals within a sample of ore, the quantity of the metals per ton of ore, and the quality of the refined ore (including the process of laboratory refinement) is done through a process known to most people as Assay. This is completed using two methods, a wet method and a dry method. The dry method was once and maybe still, is known as the furnace method. I have always heard the term as the Firing Method or simply put as the Fire Assay.

The Fire method is used to liquefy the ore into a liquid molten mass, when cooled will solidify into layers of different compounds and textures. This process of solidifying into the different layers is known as fusion. The ore is heated to high temperatures and then allowed to cool. A problem arises due to the fact that very few compounds will actually fuse on their own; without a little Alchemy. However, if you pulverize the ore and mix in certain solid reagents prior to smelting, compounds will be formed which will fuse easily at moderate temperatures. This will produce a molten mass liquefied enough to allow the heavier metals to sink to the bottom of the crucible. Those chemicals that are classified as reagents which are added to the ore to allow the non-fusible or difficult compounds fusible are generally given the term "fluxes".

Sometimes it is hard to understand the practical aspects of what does happen with the ores during firing. Therefore I will use crystal found on my claim as an example. This specimen is Auriferous Quartz. Within the specimen there was some gold diffused throughout the crystals lattice in very small or minute quantities. When crushed to a powder and heated passed the temperature of 1,064 degrees centigrade (the melting point of gold) the gold would not separate. The reason being is that the quartz is infusible. By adding sodium carbonate to the powdered ore, during the heating process, fused with the quartz to create a compound of sodium silicate which allowed the melted gold to separate and float to the bottom due to its higher density. In this case the sodium carbonate is the flux used. The resulting fusible compounds float to the surface and are known as slags.

That's not the complete story. The gold and silver particles within the quartz were so small that a small quantity of lead was used to trap the precious metals so that they would be trapped at the bottom of the crucible. The resulting metallic lead was obtained by reducing the lead oxide which was introduced into the mix. More on this subject later.

Besides the slag and the lead button containing the gold and silver, other products may also be produced. This is all dependent on the compounds within the ore at the time of fusion. If there are some metallic sulfides mixed in with the ore, an artificial sulfide would form. This layer or composition is known as regulus, also termed "matte". Now, if the ore contains some forms of arsenical minerals, a layer of speice will form. Speice is a compound or compounds of metal which contain arsenic. You will at some point in time through conversation or reading material be introduced to the term "charge". Charge is the mixture of flux and ore which is put into the crucible. If all the compounds mentioned were in the charge, they would all diffuse in layers according to their densities. See figure below. On top of the layer of slag you may find a more fluid layer of slag. This layer will usually consist of fusible alkaline, chlorides, and sulfates. The matte (regulus) is a compound of one or more metals containing sulfur. This compound will have a yellowish- grey color. Its mass will be metallic in luster and is usually brittle. It is often crystalline in structure. The speice will be hard and brittle, and will be a greyish white in color.



Crucible with contents layered after fusion

It is extremely important to use your fluxes in regards to their properties and principal uses. It is the principal uses that underlie the fluxing of your ores and references may be made regarding the actions or reactions of the various reagents that you may or will be using. There are three basic groups of fluxes that are used. These are the basic fluxes, the acid fluxes, and the neutral fluxes. Starting with the basic fluxes you have:

1. Sodium Carbonate (Na_2CO_3)
2. Sodium Bicarbonate ($NaHCO_3$)
3. Litharge (Lead Oxide) (PbO)
4. Red Lead (Lead Oxide) (Pb_3O_4) or ($PbO_1Pb_2O_8$)
5. Haematite (iron Oxide) (Fe_2O_3)
6. Lime (CaO)

Next in Line are the acid fluxes:

1. Borax (Sodium Pyroborate) ($Na_2B_4O_7$)
2. Borax Glass ($Na_2B_4O_7$)
3. Silica (SiO_2)
4. Glass

And last are the neutral fluxes:

1. Fluor-spar (CaF_2)
2. Common salt (Sodium Chloride) (halite) ($NaCl$)

Let us take a little deeper look into each one of these fluxes starting with sodium carbonate. This chemical can be purchased as an anhydrous sodium carbonate. As a powder it makes it easy to apply over and or mix with your ore concentrate. This basic flux is quickly fusible. When it is melted with silica being your quartz rich ores it fuses into a fusible sodium silicate and quickly liberates the carbon dioxide (carbonic acid) The formula is thus as shown:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

Sodium bicarbonate is used but less frequently. It contains less soda per volume than sodium carbonate. As this chemical is heated, water and carbonic acid is defused at a lower temperature and the sodium carbonate is the result as in the formula below:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

It has been proven that the bicarbonate fluxing power is two-thirds that of a carbonate. When using either as a flux, you need to heat up the charges slowly. If you heat charges quickly the escaping gasses will cause frothing and you will lose some flux due to it boiling over. This will occur more frequently when using the bicarbonate and therefore you must cut back, in other words use less in the mixture. There are two more basic fluxes that can be used so I will mention them now. The first is potassium carbonate and can be a substitute. Both fluxes when mixed in equal parts make an excellent flux and it is sometimes used in that manner. The other flux is somewhat an acid flux. They have the advantage of holding earth compounds, charcoal, graphite etc. in suspension without losing fluidity when melted.

Lead oxide is one of the more commonly used fluxes beside borax. There are two compounds of lead oxide used as a flux. These two fluxes are Litharge (PbO) and Red lead ($PbO_1Pb_2O_8$). When mixed with silica based ores (quartz etc.), when melted will form a very fusible lead silicate.

$$PbO + SiO_2 = PBSiO_3$$

Lead oxide mixed with a silicate or silicates can and will form fusible double silicates. In addition, when mixed with silicates (powdered quartz) or borax, it makes for a good flux to use for lime and magnesium. For those metallic oxides which are difficult or infusible can be easily dissolved by using lead oxides as a flux. When they do fuse they will form a very strong basic slag. However you need to know that this slag will have a very corrosive action on your crucibles. This is especially important when you mix the lead oxides with copper as it will also fuse with the silica within the crucible. You should also know that when red lead is fused, it will decompose. When fused it will give up some of its oxygen molecules converting it back to litharge. The metallic lead will remain in the slag as monoxide leaving the oxygen available for oxidation.

$$2Pb_2O_4 = 6PbO + O_2$$

As mentioned, red lead has an excess amount of oxygen and when heated during fusion will release the oxygen molecules making them available as an oxidizing agent. This is why red lead is preferred as a flux instead of litharge. It is also a good flux for trapping those precious metals as it forms as a button at the bottom of the crucible. One has to mix it with charcoal (carbon) in order to collect or reduce the lead to a metallic state. The flux will combine with the carbon particle and lose it oxygen to the carbon thereby create the carbon dioxide gas which will be vented during the fusing process.

$$2PbO + C = 2PB + CO_2$$

This is a little tip. The old timers, my friend, a chemist, Chris, and a couple of fellow from ACME a few years back told me that lead oxide also contains a quantity of gold and silver. If using this flux for assay determination of ounces per ton then the flux has to be treated as the silver content may be appreciable. As for the gold, it is negligible and be dismissed. Since so many people have told me that this tid bit is a fact then I can only assume that it is true.

Iron Oxide is usually present in most ore samples collected. It will either be in a form of Haematite (natural ferric oxide - Fe_2O_3) or more commonly as limonite which is hydrated ferric oxide ($Fe_2O_3.H_2O$). Ferric oxide is infusible; however it can be converted into a lower type of oxide by using a carbon reducing agent. Once reduced, it will fuse with silica to become ferrous silicate which will fuse easily. Now and then you may find some manganese oxides in your ore samples at times. These oxides will also act as a flux in a similar reaction.

$$2Fe_2O_3 + C = 2FeO + CO_2 \longrightarrow 2FeO + SiO_2 = 2FeSiO_3$$

Lime comes in three flavors. The first is calcium oxide (CaO), the second is calcium carbonate ($CaCO_3$), and the third is calcium hydroxide ($Ca(OH)_2$). Lime when used in the term ore is limestone. It really is calcium carbonate. When heated, the carbonic acid will be liberated leaving behind the calcium oxide. Lime in itself is not fusible, However when mixed with silica will fuse readily. This fusibility can be further enhanced by adding another base. Lime can often be found in combination with magnesium. It is formed in the mineral dolomite. It will be a double carbonate of lime and magnesia. Magnesia is hydrated magnesium carbonate. As a flux, magnesia acts in the same manner as the lime.

Calcium carbonate will also be present in some ores. It is usually found in combination with magnesium. It is found in the mineral Dolomite which is a double carbonate of lime and magnesia ($CaO_3CO_2 + MgO_3CO_2$). When used as a flux, its reaction is similar to lime.

Alumina (Al_2O_3) (aluminum trioxide) that is found in in some ores, will be found combined with silica. This compound reacts like a basic flux and is quite common in the slates and clay materials.

Borax ($Na_2B_4O_7$) is a hydrated sodium biborate. Half of its weight is water, however when heated it will lose its water. This will cause it to swell and fuse into a clear glass (borax glass). If you were going to use borax as a flux you need to make sure that the borax has been liberated of as much of its water content as possible or it could cause your charge to overflow in the crucible. You can liberate much of the water content by heating to a point just slightly above the boiling point of water prior to use. Borax is the primary flux used by most assayers and home chemists when smelting their finds. It is an acid flux. Borax contains an excess of boron trioxide (B_2O_3). That is why this flux is capable of dissolving the many metallic oxides thereby forming very fluid slags. It is also very important in fluxing those infusible substances such as lime, Zinc oxide, and more. Borax glass itself is used as a covering material for scorifying.

There are a few more items that I believe should be mentioned. Silicon dioxide (SiO_2); it is basically used in the form of a finely pulverized Quart, sometimes referred to as siliceous sand. It is used in connection with those very basic ores, especially those that have a corrosive action on the crucibles. It will combine with most of the metallic oxides or bases within the ore samples. This will form the slags which are mainly composed of silicates. It is very rarely used as most of the common ores already contain enough silica to allow the formation of the slag. Powdered glass is a good substitute for silica as it will contain a mixture of sodium and potassium silicate along with small amounts of other silicate material. Glass will usually contain about 60 to 80 % of silica in its volume.

There are two other compounds a couple of metals that should be mentioned as well. The first of the compounds is Fluor-spar and the second is compound is salt. Starting with fluor-spar (CaF), it must be pure and therefore free of any other minerals. It must be in a powdered state. It is not used that much, however, it is very suitable for fluxing calcium phosphate and other infusible silicates. It will fuse very easily with barites and gypsum. In order for fluor-spar to fuse, its temperature must be fairly high. When it does melt it becomes very fluid and has the ability to suspend any unfused metal particles without diminishing or seriously diminishing the fluidity of the slag.

The other compound is sodium chloride commonly referred to as salt (NaCl). It will fuse into a very thin fluid that does not decompose during fusion. It is typically used as a covering over the top of your samples as it will preserve some slags from oxidation. The salt should be fully dried and powdered before being used as a flux.

The two metals that I referred to is iron and metallic lead. The iron is commonly known as wrought-iron. It comes in three forms. The first is hoop iron, the second in the form of rods, and the third is nails. It is employed when the ores contain quantities of Sulphur, arsenic, and lead. The iron acts like a desulphurising agent. When your sample ores consist mainly of galena, wrought-iron crucibles are generally used.

The other metal is metallic lead, not commercial grade lead as the commercial lead has too much silver content in it. Desilverized lead is usually purchased as Assay lead or Test Lead. It is usually sold as thin sheets or in granules. Sheet lead is used in cupellation. Your ore samples or metal samples would be wrapped in a sheet of lead. Each sheet is as thin as a business card. Very pure lead can be obtained by reducing the white lead with charcoal. It takes about 100 parts lead to 3 parts charcoal powder for reduction to pure lead. Granulated lead is basically used in scorification.

I hope that that I have been able to clarify the use of the fluxes and more in this article. If you the reader has any questions, have discovered any errors, or if you enjoyed the article, please fill out the contact form in the contact section of this web site and start a conversation. Keep in mind that I too am still learning and happy smelting.