SALT II SYMPOSIA

24-25 JULY 1986

SCIENCE OF GOLD SMELTING

D. TRAINOR

HANNANS CLUB

BROOKMAN STREET

KALGOORLIE WA 6430

INTRODUCTION

Over recent years, Mint personnel have had the opportunity to visit most of the major mines in the Western Australian goldfields. This has incorporated the newer facilities such as Pancon, Mt Percy and Harbour Lights as well as older establishments such as KMA, and Central Norseman. An area of concern, particularly in the newer plants, has been the lack of understanding of furnace room procedures. The current trend appears to be to employ the latest engineering technology in all aspects of process metallurgy until concentrate is produced. Then the attitude is to load this product into the crucible, melt and cast with the result hopefully being a rough gold ingot.

Perhaps this is being too hard on design engineers and it would reflect on the preliminary metallurgical testing. However, of the enquiries currently received by the Perth Mint from the industry, 80-90% involve problems with melting technique. To some extent this is not surprising as the pyrometallurgical treatment is the completion of the primary process. However when this product reflects the overall efficiency of the mine, one would expect that a full evaluation would be done in the commissioning stage. Therefore the contents of this dissertation will centre on defining the “Science of Gold Smelting”

Fluxes

It can be seen that a differentiation has been made between fluxes and slags. The reason for this is that the fluxes are the initial constituents added to the charge for a specific purpose. The slag is the resultant product formed by the interaction of the flux recipe and the charge.

Functions and properties of fluxes – There are two fundamental reasons why a flux is used. The first is to reduce volatilisation and is achieved by using a low melting point material which itself is stable at temperatures above the melting point of the charge. At the Perth Mint, the established practise is to use a borax cover on all melts with the exception of gold casting.

The second function of fluxes is to chemically react with the charge with the object of reducing precious metal compounds into their metallic state, or to convert base metals and /or deleterious elements into a form soluble in the resultant slag. Herein lays the science of gold smelting.

Name	Formula	Properties in order of their importance.
Silica	SiO_2	Acid Flux
Glass	$xNa_2O.yCaO.zSiO_2$	Acid Flux
Borax	$Na_2B_4O_7.10H_2O$	Acid Flux
Borax glass	$Na_2B_4O_7$	Acid Flux
Boric Acid	H_3BO_3	Acid Flux
Sodium Bicarbonate	$NaHCO_3$	Basic Flux, desulphurising
Sodium carbonate	Na_2CO_3	Basic Flux, desulphurising
Potassium Carbonate	K_2CO_3	Basic Flux, desulphurising
Litharge	PbO	Basic Flux, desulphurising, oxidizing
Red Lead	Pb_3O_4	Basic Flux, oxidizing
Lime	CaO	Basic Flux
Hematite	Fe_2O_3	Basic Flux, oxidizing
Potassium Nitrate	KNO_3	Oxidizing, desulphurising
Argol	$KHC_4H_4O_6 + C$	Reducing agent, basic flux
Cream of Tartar	$KHC_4H_4O_6$	Reducing agent, basic flux
Flour		Reducing agent
Charcoal	C	Reducing agent
Lead	Pb	Collecting agent
Iron	Fe	Desulphurising reducing agent
Potassium Cyanide	KCN	Desulphurising reducing agent
Salt	NaCl	Cover and wash
Fluorspar	CaF_2	Neutral Flux
Cryolite	$AlNa_3F_6$	Neutral Flux

Table 1 Common Fluxes. (E. E. Bugbee. A Textbook of Fire Assaying. J Wiley & Sons. 1922 p13)

Table 1 shows fluxes commonly used in fire assaying and to understand the requirements of pot fusion assaying is to understand the full complexities of flux usage.

For the purpose of foundry smelting, these fluxes are the most commonly used.

Borax – comes in both hydrous and anhydrous forms and the latter is recommended as the former must lose its water of crystallisation and therefore tends to cause greater heat losses. Borax fuses at the relatively low melting point of 742^{o}C, this appreciably lowers the fusion point of all slags and it also acts as an excellent solvent for base metal oxides. The rational formula $Na_2O.2B_2O_3$ indicates an excess of acid and dissolves and fluxes practically all metal oxides, both acid and base. Borax also exhibits good fluidity in the molten state.

Silica – with a melting point of 1750^{o}C is the strongest acid reagent available. It combines readily with metal oxides to form silicates. The main problem with silica based slags is that they are very viscous and hence hold metal shot in suspension, however when fluxed with borax, borosilicates are formed. These slags still exhibit a high solubility for base metal oxides while affording control of fluidity. For further reference material on borosilicate and silicate ratios, any assaying text should be helpful.

Soda Ash – which melts at 825^{o}C is a powerful basic flux and is by far one of the cheapest available. Owing to the ease with which alkaline sulphides and sulphates are formed it acts as a desulphurising and oxidizing agent and possesses a very high fluidity. Care must be taken when using soda as a fluxing agent as an excess

will yield a very sticky and hygroscopic slag which is difficult to clean from the ingot. Also a strong soda based slag reacts exothermically with water and contact with skin can result in severe irritation.

Nitre- or potassium nitrate is a powerful oxidising agent which melts at 339^{o}C. It fuses at low temperature without alteration but at higher temperatures 500-600^{o}C breaks up giving off oxygen which oxidises sulphur and many metals, notably lead, iron and copper. A word of warning when using nitre is to control the amount required as liberation of oxygen is a vigorous reaction and apart from overflowing the crucible, will cause excessive crucible erosion. Nitre reacts with graphite according to this reaction

$$4\ KNO_3 + 5C \rightarrow 2\ K_2CO_3 + 3CO_2 + 2N_2$$

Charcoal- is used where a reducing atmosphere is required over a charge. As a general fluxing agent for the treatment of concentrates it would find very little use. However it is included in the flux list because of its obvious reducing capabilities. Carbon does not become active until a temperature of 500-600^{o}C but can be used effectively on a high copper content bullion to reduce heavy oxidation. It has been used at the Mint for this function as a heavy oxide skin can cause sampling and assaying problems.

Manganese Dioxide-is an effective oxidising agent, but more importantly has a high affinity for sulphur and is in fact used extensively in desulphurising steels. Hence if it is known that a concentrate has a high sulphide content, then manganese dioxide as a fluxing agent is most beneficial.

Fluorspar- like Borax increases the fluidity of almost any slag. How it does this is somewhat of a mystery, since its melting point of 1380^{o}C is above that normally intended for precious metal smelting. Most authorities state that it is inert and does not enter, to any extent, into combination with the other constituents of the charge.

Having now discussed the main fluxing agents, the development of a flux recipe to suit a particular concentrate becomes essential. However before pursuing this course, one must first be able to recognise the resultant products of the fusion process.

Basically what results is a metal casting and a slag phase, but depending on the amount of contamination in the charge, the flux recipe or the flux to charge ratio there are two other possible phases – MATTE and SPIESS.

Matte- is an artificial sulphide of one or more metals forming during the fusion process. It is a very low melting point phase with a relatively high density and is therefore found between the metal and slag phases, as a distinct and separate

layer. It is usually blue grey in colour, very brittle and can hold appreciable quantities of precious metal. Mattes are usually iron or copper based and contain up to 10% gold in solution.

Speiss- is an artificial metallic antimonide or arsenide formed in smelting operations, and usually iron based, however cobalt and nickel can substitute. It is a hard fairly tough, tin white substance found between the metal and slag layers, and is capable also of holding appreciable precious metal in solution.

These two phases are mentioned because as explained earlier, the formation of either is indicative of an incorrect flux recipe or flux to charge ratio. Therefore in most cases a remelt with additional flux is sufficient to eliminate either phase.

If, however, the flux recipes are at fault then matte may be broken down with either nitre or manganese and speiss with caustic soda or soda ash.

When treating material of this nature, it is usual to melt the phase first then add the fluxing agent and paddle into the molten charge. This increases the surface contact area and thus increases the reaction kinetics.

Again some caution should be taken when nitre is used in this form as severe effervescence of the nitre on decomposing can cause the material to overflow the pot. Hence when using nitre direct, it is usual to use an oversize pot. If however the charge does react turbulently, a small amount of dry salt will tend to settle the reaction down. This is simply sprinkled over the slag surface. Finally when the reaction has finished, an amount of borax equivalent to the flux used should be added. When fused, this is stirred into the charge before casting and will ensure that a manageable slag results.

A final word of warning, when adding fluxes directly to the molten charge is to make sure they are thoroughly dry or the result could be anything from severe spitting to an explosion, depending on the moisture content.

The derivation of a flux recipe is dependent on producing a slag of the following properties.

PROPERTIES OF A SLAG

1. Low Melting Point
2. High Fluidity
3. Low Density
4. High Solubility of Base Metal Oxides
5. No Solubility of Precious Metals
6. Good Separation Characteristics
7. Low Refractory Wear (Corrosion or Erosion)

In general, a vitreous or glassy appearance is the trade mark of an acceptable slag. To ensure the fastest treatment times the flux ingredients should all be finely divided and intimately mixed through the concentrate prior to loading into the furnace. This increases the surface contact area which in turn greatly assists the reaction kinetics by establishing many reaction zones in the melt.

The following general procedures are adopted by the Perth Mint when assessing a material for fusion:-

Firstly, conduct a close inspection of the material. On a mine site where the consistency of the product would be reasonably controlled, this would occur only once. However the receipts at the Mint are varied. If the concentrate has a high ash content, an initial melt with nitre mixed through the charge would be performed, with borax added towards the end of the treatment. For most other concentrates, a standard flux of:

10 Borax

4 Soda ash

2 Nitre

Borax: Soda Ash: Nitre at 5:2:1 intimately mixed on a 1:1 ratio of flux to charge would be tried. The resultant recovery would be assessed as to the properties of the slag, with particular attention given to fluidity, slag separation and crucible wear. The slag would also be assayed for precious metal content. Dependent on these factors, a correction or addition to the flux may be made. For example, if all the criteria other than crucible wear are met, then a silica addition would be made to the slag. In discussing these factors, it must be borne in mind that the Perth Mint treats relatively few concentrates and then usually less than 30 kg in weight.

	Acid Treated			**Not Acid Treated**
Borax	15	13	13	35
Silica (sand)	16	10	12	15
Nitre	-	-	-	3
Soda	-	1	3	5
Fluorspar	-	7	7	-
Manganese dioxide	1	2	2	-

Quantities in %. Remainder made up of concentrate.

Table 2. Flux recipes.

In this table of the three fluxes in the acid treated section, which flux is correct? They are all correct; each was developed by a specific mine for its own purpose and all could be a effective as each other. However, when tested to the extreme, it was found that one had marginal cost effectiveness with regard to refractory life and flux costs.

The main point of interest here is the flux ratio used for acid leached against untreated.

Acid Leached 1	39:61
Acid Leached 2	33:67
Acid Leached 3	37:63
Untreated	58:42

Zinc dust is used for precipitation.

Analysis Of The Precipitate (Dry Basis)

Gold	35.0%
Silver	7.2
Copper	1.4
Lead	9.3
Zinc	14.6
Iron	0.3
Alumina	0.5
Lime	11.7
Silica	0.7
Sulphur	4.4
	85.1

By treating the precipitate with hydrochloric acid a residue of gold, silver and copper with only small amounts of other elements is obtained.

Analysis Of The Residue (Dry Basis)

Gold	75.85%
Silver	15.37
Copper	2.27
Lead	0.15
Zinc	1.54
Iron and Alumina	0.14
Lime	0.32
Silica	0.46
Sulphur	0.76
	96.86

Table 3. Acid Treatment of Concentrate.

Note that the gold and silver percentage improved from 42.2 % to 91.2 % on a dry basis.

The reason for showing these figures is because of the trend to go to direct smelting of loaded cathode. If the process control on all sections of the plant is monitored so that consistent solution head grades are fed into the electrolytic circuit then running a known cathode weight for a set time is fine. The flux recipe can be designed to cater for residual base metal and some tolerance in the solution head grades can be absorbed. However if there is a significant drop in the grades, then the cathode will retain more base metal, which will not be effectively removed by the smelt. Should head grades fluctuate constantly, then the life of the gold room foreman is made much more difficult. On CIP recovery circuits it is recommended that a post electrolysis leach is performed on the cathode material for the three reasons listed.

1. Makes fusion easier and more controllable.
2. Residual base metal incurs higher refining charges.

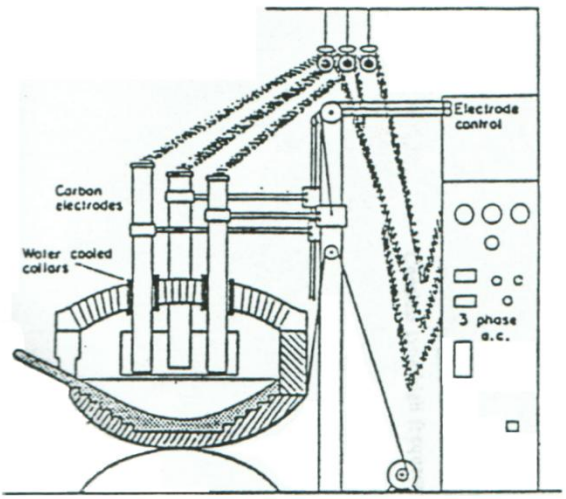
3. High base metal content can affect the homogeneity, resulting in inaccurate assay results.

For steel wool cathodes, hydrochloric acid is recommended and for aluminium, caustic soda. It is understood that several mines are now experiencing much higher copper concentrations once they get into the sulphide zones of the ore body. To this end, it is essential that if the copper is removed that this should be done hydrometallurgically at some stage prior to smelting. This point is made as it has been the experience of the Perth Mint that where copper is oxidised pyrometallurgically and absorbed into the slag, that significant quantities of gold are co-transported to the slag. One such test on an alloy of one third gold, one third silver and one third copper using oxygen injection and a borax slag, resulted in approximately 10% of the gold being dissolved into the slag.

Furnace Technology.

There are three general energy sources, electricity, oil and gas, used in melting technology. In the electrical section, the subdivisions are arc, induction and resistance furnaces. Resistance furnaces generally are only ovens and as such they offer little advantage over conventional fired furnaces.

Arc Furnaces.

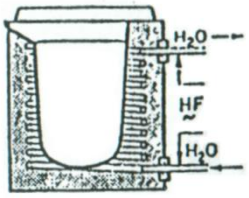


Hall-Heroult type three phase direct arc melting furnace as used for steelmaking. Electrode positions are continuously adjusted. Charging may be via doors or through a removable roof. Furnace tilts for slagging and casting.

Fig 1 Electric Arc Furnace.

Arc furnaces are commonly used by major mines in South Africa. They comprise of three carbon electrodes which are submerged into the charge and an arc struck. The furnace capacity is typically 750 kg of material smelted at temperatures up to 1400^{o}C in cycles of 3 hours duration. The furnaces operate at 600A with electrode life of 35 smelts or more are typical. The capital cost of these furnaces is very high and no mine in Australia would be expected to warrant such a facility. An interesting comparison to Australian mines is the Harmony Mine in South Africa which employs 37,000 people and operates two such furnaces continuously.

Induction Furnaces.



Coreless type high frequency induction melting furnace

Fig 2 Induction Furnace.

Induction furnaces use the principle of pulsating electromagnetic fields around the furnace coil. The frequency of the field is matched to the charge to induce heat by excitation of the atoms. In this manner, the furnace has very fast melt times as the heat is generated directly in the charge and hence does not rely on preheating the refractory material and the crucible. Induction furnaces can also have the furnace frequency tuned to generate heat in the crucible similar to an oil or gas fired furnace, where the heat transfer to the charge is by conduction and radiation from the crucible and furnace lining. This method is used for non-inductive charges, i.e. where sufficient heat can't be generated in the charge to cause it to melt. In this application, it could be questioned as to whether the significantly higher capital investment and maintenance costs are warranted. The tendency of this type of application is to reduce crucible life and hence costs. However, the larger the capacity of the induction furnaces make the application a cost related study if considering such a melting medium and as such is directly proportional to the size of the mine.

Oil and Gas Fired Furnaces.

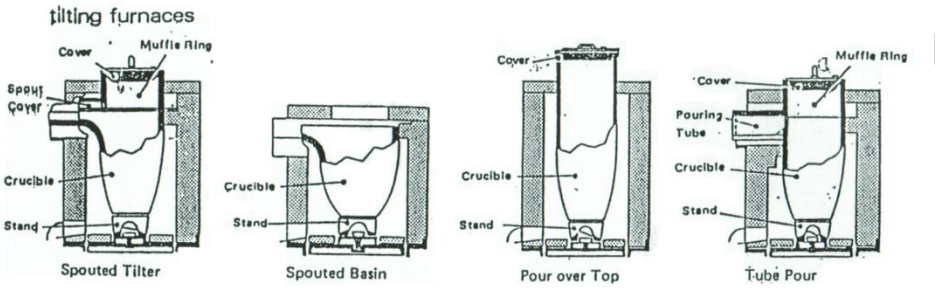


Fig 3. Oil and Gas Furnaces.

Oil and gas fired furnaces are recommended for smaller mines where the melt cycle is on a weekly basis. These furnaces are much cheaper to install and in general maintenance can be handled on site by mine staff. Furnace design can vary from cylinder, to rotary, to tilter construction. The cylinder furnace or pit furnace is fully manual with the crucible being lifted from the furnace to pour. The rotary furnace is used for medium sized smelts of cyanidation concentrates and the rotary action affords good mixing and contact of the charge and flux during smelting. The tilting furnace is the type generally favoured, as it reduces the labour requirement to load and pour. On large pours, cascade moulds can be used where the slag over pours the first mould into the subsequent mould until the pour is complete.

Refractory Technology

Crucibles.

In general there are two main grades of crucible material: clay graphite and silicon carbide. Of the two, silicon carbide is in most instances the more durable especially where corrosive fluxes such as nitre are concerned. However, they are more expensive than the clay graphite and this is another instance where some experimental work in the furnace room on refractory wear could result in substantial savings. This also gives the incentive to investigate the flux recipe and flux charge ratio in order to ascertain the best smelting conditions.

Clay crucibles are also available and have some special applications, particularly when trying to remove large amounts of deleterious material. The advantage of the clay or clay lined crucible is that it is carbon free, hence when base metal is oxidised it is dissolved into the slag and won't reduce back from the carbon content of the crucible. It is also important to bear in mind that there is currently at least three brands of crucible available in WA.

CRUCIBLE AND REFRACTORY SUPPLIERS

CRUCIBLES

Brand	Supplier
Morgan	Mathews Metals
Noltina	Inductotherm
Mars	Elsewhere Engineering

REFRACTORIES

Mathews Metals
Nonporite
Sila
Refractory Installations
Norton

Table 4. Crucible and Refractory Suppliers.

This is significant in that each manufacturer uses a different refractory formula and sources the materials from various locations, so that some brands may be more suitable for your application than others. The same applies to refractory cements, rammable and mouldable refractories etc.

The names in the list are by no means a recommendation in any order of preference but are listed to give an indication of the range of alternatives available.

Moulds and Mould Dressings.

It is generally accepted that a grey cast iron, SG (spheroidal graphite) cast iron or meehanite are the best materials for moulds, however mild steel would suffice. The advantage of cast irons is that they are more resistant to thermal shock and to some extent are self dressing due to their high carbon content. However, it is not recommended to use the undressed, as the carbon will burn out causing embrittlement of the mould. The reason a mould is dressed is to allow an easier de-moulding process so the properties of the mould dressing should be low thermal conductivity, adherence to the mould surface and resistance to decomposition or thermal break down during casting. To this end, carbon based dressings are usually preferred and some common applications are:

Mould Dressings

Oil, kerosene, acetylene or turpentine smoke, lamp black in suspension in turpentine, lubricating oil wiped over the mould surface, linseed oil (usually broken down with kerosene) or neat's-foot oil (usually broken down with kerosene)

* A suspension of Dixon's Air Spun Graphite in diesel painted on the mould and heated on the side of the furnace also works very well.

*Solid carbon moulds are also available and do not require dressing, release the ingot easily and are very light. They can however be brittle compared to cast iron moulds and need to be handled with appropriate care.

In preparing a mould for casting, the mould should first be preheated to drive off any moisture, this is very important as residual moisture will cause the casting to explode. The mould is then dressed. With the practise employed generally of allowing the mould to fill with slag and then over flow into a tray, it is suggested that the initial mould temperature should be quite cool, as constant pouring into one section of the mould causes overheating of the surface resulting in burning through the dressing and this is reflected in deep porosity of the casting. In the most severe cases, the casting may even weld to the mould face thus causing extreme difficulties in removal, and most probably destruction of the mould. Incidentally, the Perth Mint prefers to receive ingots of no more than 12.5 kg (400oz) in weight, as this facilitates our loading mechanism and crucible size, however if you are customers of our opposition, then cast them as big as you like, until they complain.

A further area that could be beneficial to explore is to sample the fumes generated during the smelting operation and assay for precious metal content. In South Africa all facilities visited had bag house filtration of the extracted fume. Efficient fume extraction will also help control dusting losses when adding materials to the crucible during fusion. In these instances, the fine particles are caught in the thermal thrust of a gas or oil fired furnace and are then distributed all over the foundry floor. Therefore it is urged that fume samples are taken so that an evaluation of the necessity to contain the fume generated can be made.

*Bagging of mixed concentrate and flux in new or old calico sample bags for addition to the furnace reduces dust losses significantly when compared to pouring the mixture directly into the pot. The bags burn down to carbon which can be fluxed out with a proper flux.

*These notes were added to the text and not presented originally.

SMELTING

1.0 Summary

Doré containing substantial levels of iron has a high melting point and is hard. The former makes smelting difficult while the latter, causes problems in drilling samples for analysis and also in stamping identifying marks onto the bars.

Mints have in general not been happy to accept doré containing much over 20/1000 parts iron (assessed by attraction to a magnet), as this causes segregation which prevents good sampling. Furthermore such doré tends to spit in an induction furnace.

The direct smelting of doré loaded steel wool cathodes avoids the steps of dissolution, decantation and filtration of a corrosive slurry which at smaller operations lacking engineered facilities, can be messy, noxious and labour intensive. Furthermore, the removal of iron by acid washing has often proved ineffectual, particularly where low plating densities have lead to the formation of coherent gold plating.

To date, the two major problems of direct smelting have been the need for high flux additions and an inability to balance the fluidity and aggressiveness of the slag.

Minor problems have included a tendency to foam (allowing only a small fraction of the crucible volume to be used), stabilising an emulsion of doré in the slag phase (by surface charge as well as viscous drag effects), poor doré/slag separation (due to enamelling), and failure to sufficiently remove iron (probably due to insufficient oxidation or mildly reducing conditions).

This monograph provides the background to development of a flux, which forms a slag that behaves well during melting, pouring and separation from doré.

The flux comprises 47% sodium nitrate, 42% silica and 11% fused borax. Where anhydrous boric acid is not available, the recipe must be modified to 43% sodium nitrate, 39% silica and 18% boric acid. The major innovations with respect to conventional wisdom is the avoidance of soda ash, fluorspar and pyrolusite (MnO_2) and the used of fused borax (anhydrous boric acid B_2O_3) rather than borax (sodium tetra borate $Na_2B_4O_7.10H_2O$). Furthermore use of sodium rather than potassium nitrate is advised, the presence of moisture in the crucible charge should be avoided.

At an addition of merely 1 to 3 kg flux per kg steel wool, the flux will generally produce doré buttons containing 3/1000 parts iron from doré loaded steel wool cathodes containing even up to 70% iron, while providing a clay-graphite crucible life of around 40 smelt campaigns.

Notes on bullion pouring, troubleshooting and preferred kiln, crucible, heating and insulating hardware are also included.

The key conclusions are that the melt should be kept at 950^{o}C and occasionally paddled until the bulk of the iron has been oxidised and taken into slag. Thereafter the temperature should be increased to 1100^{o}C, and poured as soon as the melt is the consistency of honey and is homogenous.

2.0 Direct Smelting Of Cathodes

However, gold metallurgists at smaller operations have been attempting to move away from acid washing of steel wool cathodes prior to smelting in order to avoid the messy, noxious and time consuming intermediate steps of dissolution, decantation and filtration of corrosive slurry.

At larger operations more sophisticated provisions have been warranted, which ensure that the operation can be rapidly and easily carried out.

The trend to direct smelting at most operations applying Zadra elution has been further accelerated because of poor efficiency of acid washing where coherent gold filming protects the steel wool from effective acid attack. Such coherent gold films have proved common both at smaller operations where the electroplating current density is generally low e.g. under 10 A/m^2, and where Zadra elution ensures a highly favourable electrolyte resistivity e.g. under 0.2 Siemens.

Operations treating ores high in silver generally also favour a move away from acid treatment because of the significant risks of dissolving and losing silver in the presence of chlorides and oxidants.

The attractiveness of direct smelting of cathodes has been greatly improved by the development of electrowinning cells that allow gold loadings in excess of 4.5 kg Au/ kg Fe. These loadings are achieved by using thin cathodes and parallel electron and electrolyte flux. Less than 20% steel needs to be slagged off loaded cathodes produced in such cells.

Another advantage of direct smelting is that the amphoteric nature of iron can be exploited, to form slags less aggressive to crucible walls.

According to Laatsch (1925), the pyrometallurgical refining of gold from steel is generally conceded to be so onerous that hydrometallurgy is advised when there is more than 80% steel. Goldroom smelting practice indicates that pyrometallurgy might even be impossible if the gold concentration is too low. This is in contrast to Barcza (1985) who reports that methods of phase concentration of gold by pyrometallurgy which can provide 99.5% recovery from feedstock containing 20 ppm gold have been developed.

However, attempts to direct smelt loaded steel wool cathodes have met with limited success, principally because earlier flux recipes which were drawn on were developed to

treat oxidised iron in the form of heavy iron minerals, or rust flakes captured by gravity equipment. In contrast the iron contained in gold-loaded cathodes needs to be converted to the ferrous or ferric state before it can be slagged. The requirement to provide for the oxidation of iron if it is to be successfully slagged forms the basis for adding oxidants or providing for in-situ oxidation e.g. by air injection. It is convenient to add sodium required for fluxing as nitre to promote oxidation.

In fact some Rand gold operations where the existing Goldroom contains a calcine furnace, the steel wool is calcined prior to smelting as an alternative to in-situ oxidation during smelting. This has allowed the operators to apply the recipes originally developed for smelting concentrates containing iron minerals and rust.

It is the same need to oxidise iron that mitigates against the use of soda ash which is a mild reductant, as a flux. (The tendency for soda ash to cause foaming due to rapid gas generation is also undesirable).

The development of a suitable flux for loaded steel wool cathodes can be achieved by providing for the abovementioned iron oxidation, as well as for the other features desired for a flux, namely that it forms a slag which:

- Partitions the bulk of the non-precious metals into the slag phase
- Has a low melting point
- Does not attack the crucible at an excessive rate
- Has a low viscosity
- Limits volatilisation of molten metals
- Separates easily from doré button after solidification

This monograph discusses the major features and development of a flux to direct smelt doré loaded steel wool cathodes.

3.0 Forming Low Melting Point Iron Eutectics

The steel wool generally constitutes the major impurity to be removed. The removal of iron thus forms the basis for developing a flux recipe.

A ternary diagram developed by Bowen, Shairer and Willens (1930) indicates that a ferrous alkali slag, $2[Na_2O.SiO_2].[Fe_2O_3.2SiO_2]$ which melts around 900^oC (See Fig 1) provides a low melting point aegirine/waterglass eutectic, and can thus be applied to slag off steel wool.

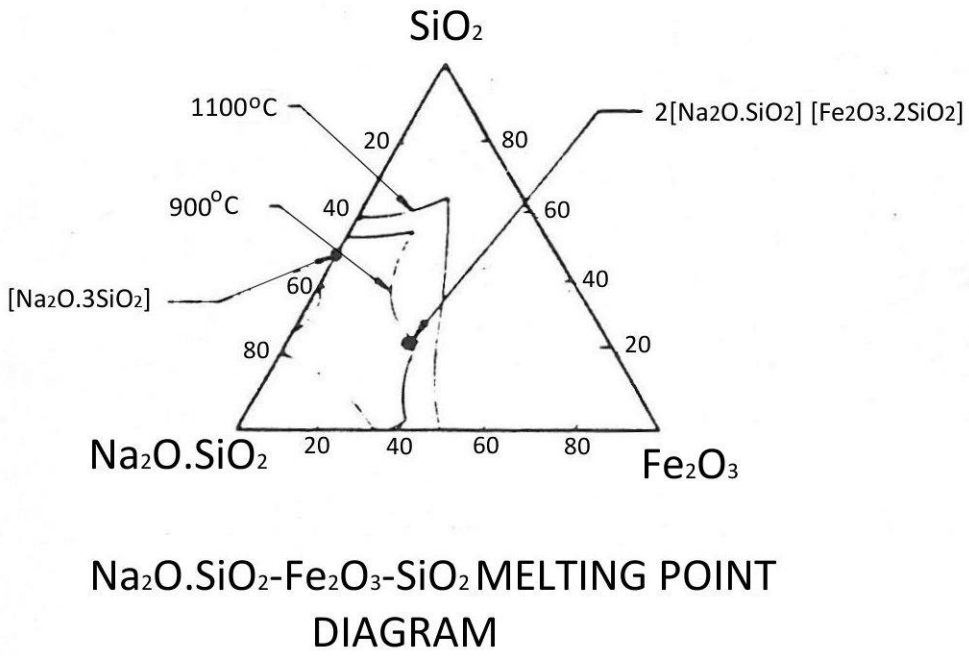


Fig 1. $Na_2O.SiO_2$-Fe_2O_3-SiO_2 Melting Point Diagram.

The choice of the above point on the ternary diagram has been chosen in order to achieve a maximum uptake of Fe_2O_3, while ensuring a slag melting point around 200°C below that of doré (a factor known from practice to be necessary to provide a good slag), and also to maintain a maximum SiO_2 content (in order to limit basic attack on the crucible as discussed further on).

Table 1 below gives the flux recipe which may be derived from the above, applying the minimum quantity of Na as $NaNO_3$ to achieve the desired oxidation of iron.

Alkali Flux Recipe	
$NaNO_3$:	60%
SiO_2:	40%

Table 1 Alkali Flux Recipe.

In a melt, $NaNO_3$ provides 1.5 O^{2-} (the rest escaping as NO). Thus 5.2 kg of this flux, which is stoichiometric with kg steel wool is forming the aegirine/waterglass eutectic, provides two times the stoichiometric quantity of oxygen needed to oxidise iron to the ferric state.

In practice this slag has proved fairly nonaggressive to the crucible. However it is viscous, and some of the gold swept into the slag phase by turbulence during the pour forms shot in the slag as it is not released back to the button before solidification.

A gold-iron phase diagram derived from data of Seigle (1956) is shown in Figure 2 and illustrates a number of features important to removing iron from gold.

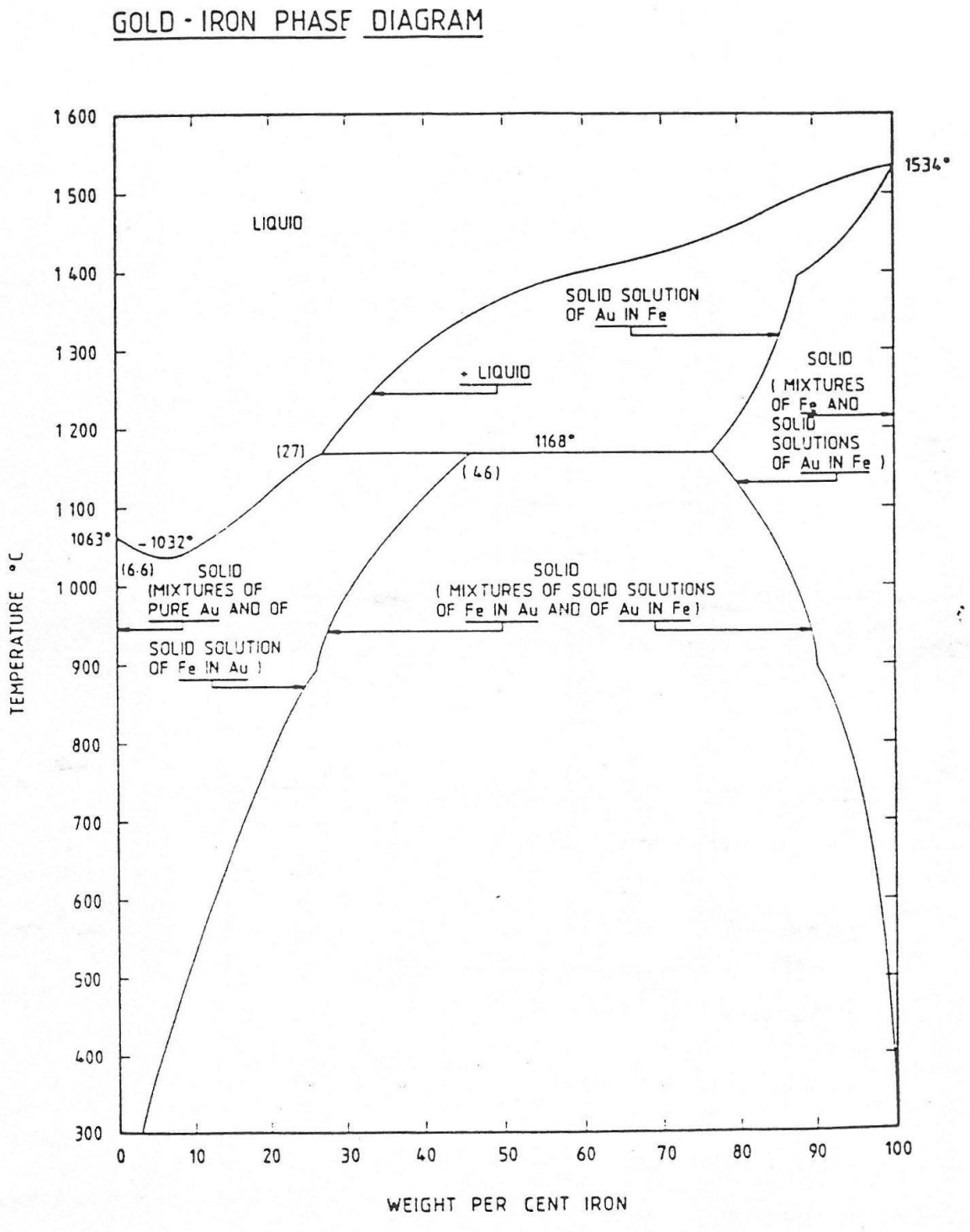


Figure 2. Gold Iron Phase Diagram.

Firstly no more than 27% Fe can be tolerated when gold melts to avoid inclusion of refractory high-iron solid phase components in the bar.

Secondly, no more than 3% Fe must be aimed for if the risk of a second iron-rich phase within the bar is to be totally avoided when the bar is poured.

These requirements dictate that the gold must not be melted (and thus be able to take up metallic iron) until the bulk of the iron has been oxidised and drawn into the slag phase.

This is conveniently done by keeping the melt at 950^{o}C and occasionally paddling until the melt is uniform.

Thereafter the temperature can be taken to 1100^{o}C and the melt poured as soon as homogeneity is achieved and the slag has the consistency of honey.

Although prior oxidation (calcination) of steel wool is applied, this step is not essential. The prior oxidation of iron reduces the risk that insufficient oxidant has been added, or is lost prior to use or is used in attack of the crucible carbon.

However, sufficient time must still be provided to allow the iron to be taken up into the slag phase, and care must be taken not to use excessive temperatures or carry the smelt on too long with the consequent risk of reduction of the iron to metal by crucible carbon.

4.0 Forming Borax Glasses

Bugbee (1940) records conclusions of T.K. Rose that an optimised borosilicate flux suitable for slagging many metals comprises:

$2[Na_2O.2SiO_2].2[2B_2O_3.SiO_2].3SiO_2$

Traditionally when slags of this type have been aimed for, boron has been introduced as borax

$[Na_2O.2B_2O_3.10H_2O]$.

However to provide maximum oxidising potential, the flux may be made from sodium nitrate and fused borax according to the recipe given in Table 2 below.

The application of fused borax (B_2O_3) as a boron source has proved to be the key for the development of the most successful mixed flux revealed in the next section. According to Weast (1979/1980) fused borax has a low melting point, and Singer and Singer (1963) record that it has a particularly low surface tension. Consequently it will wet the steel wool and engulfs undissolved flux reagents during the initial stages of smelting, serving as a medium for slag reactions to proceed in.

More importantly, all the boron added as fused borax is available to interact with metal oxides in the melt, unlike borax which has already to some extent satiated the oxygen bonds with the associated sodium. Sodium introduced with borax would not only be an unnecessary diluents which does not contribute to the reactions required (e.g. iron oxidation), but serves to take up some of the bridging capacity of the boron which could otherwise be expended on iron. Sodium being a strong base would also increase reactivity of the slag towards the crucible.

A further advantage of fused borax is that it does not introduce water, (even as water of crystallisation as in borax, $Na_2O.2B_2O_3.10H_2O$ or as bound water in boric acid, $B_2O_3.3H_2O$ which contain 47% and 44% water respectively) into the melt. Such water can promote the loss of the oxidising power of $NaNO_3$ by allowing volatile HNO_3 to form and be driven off while the crucible charge is heating up.

The final reason for preferring the fused borax is that it does not contribute to loss of heat through volatilisation of contained water.

Mk 1 Non-ferrous Metal Flux		
SiO_2	:	46%
B_2O_3	:	24%
$NaNO_3$	:	30%

Table 2 Mk 1 Non-ferrous Metal Flux.

150 g of this flux is used per g-mole of RO metal oxides, and 230 g per g-mole of the R_2O_3 metal oxides. This corresponds to 1.8 kg flux per kg Fe in the ferric state, and 2.3 kg flux per kg Fe in the ferrous state. Further quantities of this flux are added to remove base metals such as Cu and Ni from doré.

This flux has proved to be of acceptable fluidity, but is unfortunately reasonably aggressive towards the crucible.

This flux has a melting point of 850^{o}C, which is well above the minimum which may be derived from Levin, Robins and M.C. Murdie (1964). On their Na_2O-B_2O_3-SiO_2 phase diagram, a “sweet spot” flux melting at under 600^{o}C may be derived. The composition is given in Table 2b below and corresponds to

$$6[Na_2O.2SiO_2].7[2B_2O_3.SiO_2].$$

It should be noted that the stoichiometric excess of $2B_2O_3.SiO_2$ over $Na_2O.SiO_2$ is very important to achieve a low melting point. This slag would be very aggressive towards crucibles, until it has taken up a substantial quantity of iron.

Mk 11 Non-ferrous Metal Flux		
SiO_2	:	40%
B_2O_3	:	34%
$NaNO_3$	:	26%

Table 2b Mk 11 Non-ferrous Metal Flux.

5.0 Mixed Fluxes

It has proved possible to combine the best features of the above fluxes, and avoid the worst, by using a mixture of them. However the use of a greater number of slag components affects both the melting point and the vitrification of the slag.

In general it is desirable to aim for the highest and sharpest melt transition temperature range, consistent with adequate fluidity for the pour, and experience to date indicates that incorporating an excessive number of slag components prevents achieving this aim.

The determination of a preferred flux composition comprising both the aegirine/water glass eutectic shown in Figure 1 and the borax glass as proposed by T.K. Rose has provided a reasonably satisfactory compromise.

In this regard a number of plant–scale experiments has led to the development of a flux of composition first published in a paper by the author of “Heap Leaching”, given at the AusIMM Regional Conferences on Gold Mining, Metallurgy and Geology at Kalgoorlie October 9-11, 1984. An improved composition is given in Table 3.

Practical Flux For Loaded Steel Wool Cathodes		
	(a) If B_2O_3 is available.	(b) If H_2BO_3 is available.
$NaNo_3$	47%	43%
SiO_2	42%	39%
B_2O_3	11%	18%

Table 3. Practical Flux for Loaded Steel Wool Cathodes

Added at the stoichiometric rate of 3.1 kg flux as per Table 3 (a) per kg steel wool (to slag 25% of the iron as Fe2O3 with flux of composition given in Table 1, and 75% of the iron as FeO with a flux of composition as given in Table 2) to produce doré containing as little as 2/1000 parts Fe. (Note steel wool loaded to around 8kg doré to 1kg Fe). Even flux additions as low as 1kg flux per kg steel wool have provided acceptable doré (viz. having around 3/1000 parts Fe), however requiring increasing temperature, and creating a relatively viscous and slow congealing slag.

6.0 Oxidative Attack On Crucibles

The carbonaceous components of ordinary clay/graphite as well as of the silicon – carbon bonded clay/graphite crucibles generally applied for smelting doré are subject to oxidative attack.

It stands to reason that the addition of the minimum quantity of oxidant, to the extent merely of achieving the oxidation required in the melt, will minimise oxidative attack on the crucible. Thus the quantity of initial alkali flux can be fixed to achieve stoichiometric in-situ oxidation.

However because of thermal decomposition of the nitrate, some nitrous oxides inevitably escape from the slag before giving up all their oxygen. The extent of this inefficiency is determined inter alia by melt temperatures, less fluid slags and deeper crucibles (see Bugbee 1940), predictably leading to a closer approach to stoichiometry.

Any oxygen deficiency can be further made up by introducing atmospheric oxygen which may be adsorbed at the slag surface or injected into the melt with a lance, avoiding impingement on the crucible walls. Merely $1m^3$ air provides sufficient oxygen to oxidise 1 kg Fe. Note however dry air (e.g. from an instrument air line) should be used to avoid explosive steam generation in the crucible.

Air injection stirs the melt, promoting slag reactions (and crucible attack). However adequate stirring can occur without air injection (by thermal convection as well as by in-situ gas generation) particularly if the flux viscosity is kept reasonably low. (A modification to achieve this is discussed in a later section)

On balance it is probably most practical to avoid much reliance on atmospheric oxygen as surface adsorption is slow while air injection requires some dexterity and complicates the process. Note that lower oxygen solubility at higher temperatures could reduce the effective oxidation of the steel wool.

Should further nitrate additions be desired to improve in-situ oxidation it is desirable to add this with sufficient silica to form the low melting point (under 800^oC) and non aggressive acid eutectic $Na_2O.3SiO_2$ (see Figure 1) The relative proportions of the oxidant powder should be as given in Table 4.

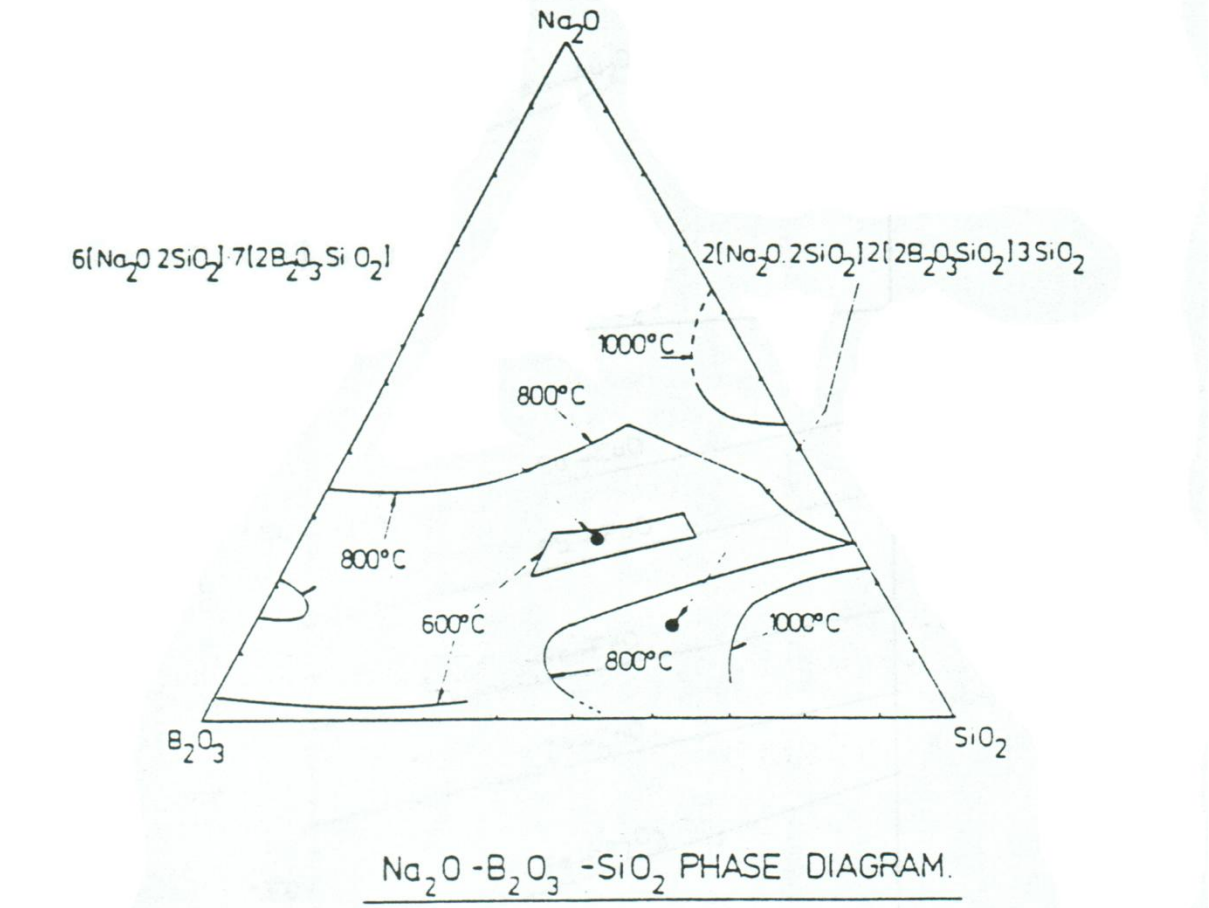


Figure 3. Na2O-B2O3-SiO2 Phase Diagram.

Figure 3 from Levin, Robbins and McMurdie clearly demonstrates the dangers of deviating substantially from the suggested eutectics (and corresponding tie lines) for example by adding $NaNO_3$ alone: higher melting and viscous slags can easily result.

Composition of Non-aggressive Oxidising Powder

$NaNO_3$	: 50%
SiO2	: 50%

Table 4. Composition of Non-aggressive Oxidising addition.

0.7 kg of this flux will provide stoichiometrically for the oxidation of 1 kg of Fe to Fe_2O_3

The need for more in-situ oxidation is most likely to arise if significant quantities of non-ferrous metals are recovered with the bullion during electrowinning. In such cases it may be convenient to compound a single flux to both oxidise and slag these metals. The recipe given in Table 2 will achieve this.

Paul (1986) warns against the use of excessive quantities of nitre, which could lead to the oxidation of silver and its loss to the slag phase.

Trainor (1986) warns to add the nitre slowly if used to supplement a hot charge due to the risk of excessive foaming, following rapid gas release (noting though that a small amount of dry salt sprinkled over the slag surface will tend to settle the reaction down).

7.0 Basic Attack on Crucibles

The tendency of alumina and silica to be dissolved into the slag phase increases as the quantity of oxygen rises above that required to form tri and tetravalent ionic oxygen bonds which transform the clay minerals from their crystalline state to a polymeric melt.

The relative quantity of oxygen excess or deficiency to satisfy the requirement for ionic glassforming bonds may be estimated from

$$Z=[n_{(M_2O+MO)}+3Xn_{(A_2O_3)}-3n_{(N_2O_3)}-2n_{(N_2O)}]/[6n_{(N_2O_3)}+2n_{(N_2O)}]$$

Where n = the number of moles of the respective oxides denoted by the various subscripts.

M = true metals (alkali and alkali earths, base and divalent ferrous metals)

A = amphoteric metals (trivalent ferrous group metals)

N = non metals (Al, Si, B)

Using the Lewis concept of describing potential electron donors as acids (Condurier, Hopkins and Wilkomirsky [1978]), the metal oxides may be described as basic and the non-metal oxides as acidic flux or slag constituents.

Following Grimshaw (1971) one may expect X to tend to -1 in a very basic slag, and to +1 in a very acidic slag. Possibly a buffer effect is set up by amphoteric constituents in a slag of intermediate acidity.

Negative values of Z denote an acid slag, not prone to attack the fire clay Si or Al constituents of a crucible wall, or the silicon held as carbide (SiC) in that type of crucible. However the more positive Z becomes, the more aggressive the slag attack will become.

8.0 Pouring The Bar

Trainor (1986) recommends grey cast iron, spheroidal graphite (SG) cast iron or meehanite because of their resistance to thermal shock and the self dressing characteristic imparted by their high carbon content.

However as the burn-out of carbon from the mould metal will cause embrittlement, dressing with lamp black and/or an oil wipe is recommended (silicon spray has also been

successfully applied as a dressing). This should be done after heating the mould to about 150^{o}C. The main purpose of this heating is to ensure that no trace of moisture is present (e.g. by hygroscopic adsorption onto trace oxides left from a previous smelt), to prevent spitting when the charge is poured. Excessive heating of the mould should be avoided as this can lead to burn-through of the dressing during the pour.

To prevent burning through the dressing, and in extreme cases welding the bullion to the mould, the pour should be gentle and preferably played along the whole mould and not kept at one spot.

9.0 Slag / Doré Separation

Enamelling occurs by interphase metal bonding which occurs when the same metal is present in substantial quantities in the bullion (where it is in the metallic state), and in the slag (where it occurs in the oxide state).

Thus enamelling will typically occur when insufficient oxidation of base metal or iron, or excessive oxidation of silver has occurred. As can be seen from Fig 4, Cu is potentially the most troublesome substance, and it is no surprise to recall that the art of enamelling is generally based on copper. The enamel furthermore holds and will not craze or peel off the bullion if there is little differential expansion on cooling.

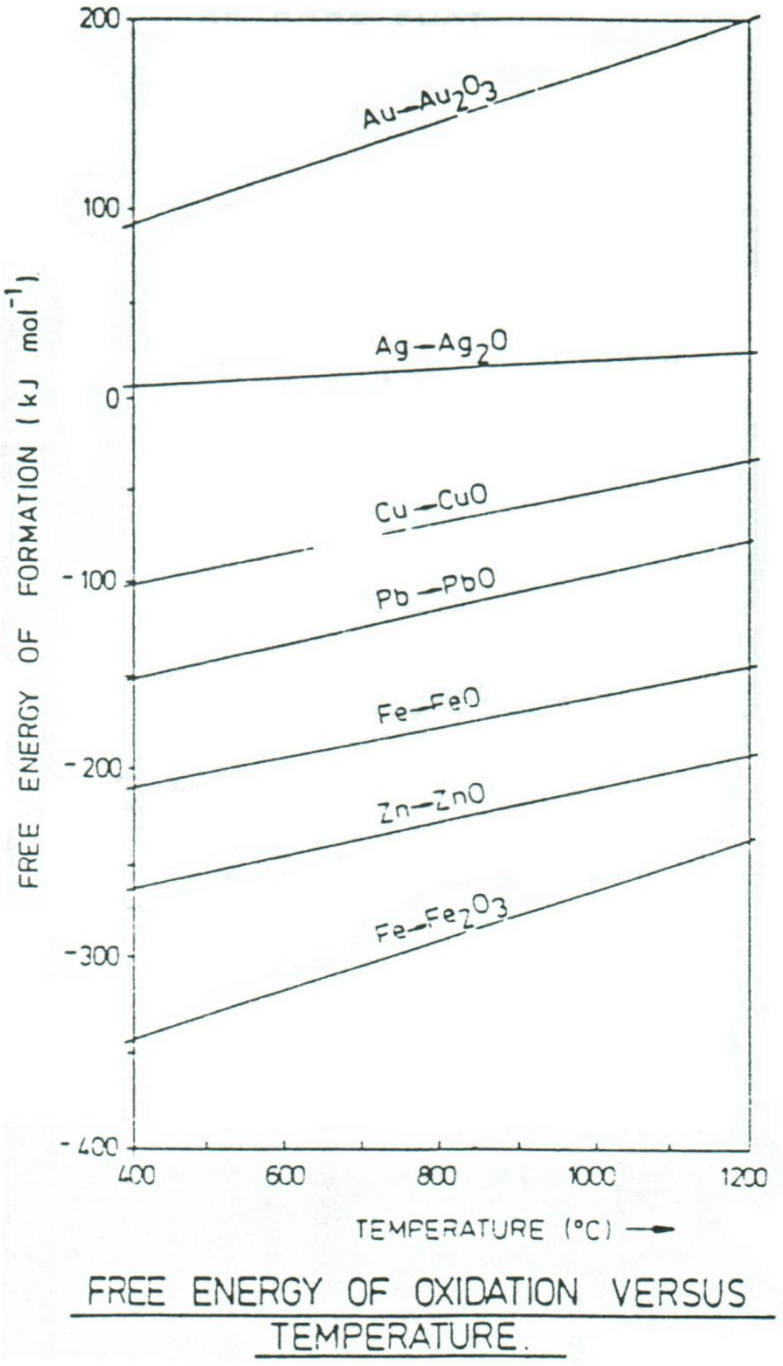


Fig 4. Free Energy of Oxidation.

It is expected that the slag, being a glass, will not be brittle above 400^{o}C. During cooling to this temperature it is thought that differences in the thermal expansion coefficient between doré and slag will not lead to slag/doré separation.

By calculating (for example using methods given by Vargin [1967] and Shaw [1971], the linear shrinkage of the doré, and the slag, and the modulus of elasticity, compressive strength, tensile strength and shear modulus of the slag, it may be estimated whether

reasonably good and consistent separation of the slag from doré may be expected after solidification and cooling.

An interesting conclusion derived during the test work applied to develop some of the slags presented in this monograph, concerns a need to avoid adding too many slag components. Whereas the synergistic increase in the depression of melting point when a larger range of flux components are used (to respectively flux ferrous and non-ferrous metals) would be thought to be an advantage, the increase in vitrification range of the slag resulting from the use of a larger range of flux components is generally a greater advantage, as this decreases the propensity for the slag to spall from the doré on cooling.

Two approaches are available to recover gold shot from doré:

Where abundant crucible operating time is available, the slag can be remelted. (Lead can be used to assist in the collection of shot, and further refining [scorifying] proceeded with as for fire assaying.)

However, if more than one normal melt is done per shift, it could provide desirable to break up the slag (large metal pestle and motor or dolly; or hand roll [metal rolling pin] in pan), recover the coarse shot by hand picking and the fine shot by tabling or hand panning. Mere wetting slags leads to their substantial decrepitation and this may be worth trying. * Note another method can be to return slag removed from the top of all the bars into the next melt for re-smelting. This slag often contains more shot than the slag that has overflowed the mould.

Note that slags contain large quantities of hydrated caustic and can be very corrosive to hands, eyes, etc.

The residual slag from secondary enrichment is often thrown into the mill feed. However, it is probably better practice to drum it and leave it for special treatment campaigns at the end of the project life when final clean-up is made. * This is not necessarily the case, circuits with centrifugal gravity recovery are often very efficient at visible gold recovery and in some instances significant gold can be locked up in these slags, the value of which is better realised sooner rather than later.

10.0 Troubleshooting

Some aspects of troubleshooting which have recently been recorded by Hinds and Trautman (1983) are included in the discussion below in order to provide a more complete overview.

Inappropriate flux formulation or inadequate flux quantities are shown up by changes to the doré and/or accumulation of base/ferrous metals at the doré slag interface as well as dullness or accumulation of graphite on the slag surface. The character of the slag is also affected.

Graphite on the slag surface is indicative of excessive crucible attack, which is often mechanical, e.g. due to rough stirring or bubble generation at graphite flake attachment points along the crucible walls. Chemical attack, e.g. due to excess oxidant or acid slag, naturally exposes more graphitic flakes. The excess oxidant can be due to an excess of flux "per se" as well as insufficient oxidant demand due to prior calcinations of the steel wool.

As has been mentioned, iron in doré makes it hard and magnetic. Copper makes it brassy. Furthermore nodular accretions of these metals generally form at the slag/doré interface (when they have not been adequately fluxed) and are generally easy to recognise. When larger quantities of non-bullion metal accumulate at the slag/doré interface, enamelling (sticking of slag to the metal) can also occur.

An inadequate quantity of flux is also generally saturated with the oxides of the doré diluents (generally Fe, Cu, Ni), which all react basically. Such basic slags are generally dull rather than shiny, and retain doré.

The high proportion of diluent oxides overlaying diluent-rich doré in an inadequately fluxed smelt, tends to enamel well (adhere slag to doré). Vargin (1967) states that this occurs because of the good bonds that can form between a metal and its oxides, a phenomenon enhanced by the tendency of the lighter doré diluent metals to concentrate due to their lower density, at the top surface of the doré.

A viscous and lumpy slag may result from inadequately fluxed or un-oxidised iron, or inadequate temperature. Lumps of incompletely slagged iron may be expected to sediment to the bottom of the crucible, and should be mixed with extra oxidising powder if needed, using a rod. The rod should be spatulate and used as a paddle to avoid crucible damage.

More oxidising powder can be added to supplement atmospheric oxidation. However excessive flux additions leading to crucible attach (observed by crucible wall erosion as well as graphite coating of the slag surface) should be avoided. An excess of flux can also lead to a reddish haematite-rich flux that tends to enamel to the doré.

It is important that the crucible charge be as dry as possible, as oxidising potential can otherwise be lost during heating as nitrate combines with boric acid, forming HNO_3 which is fumed off at temperatures below $125^{o}C$.

Bringing up the temperature too fast can increase the risk of melting the contaminants into doré from where it can only be fluxed out with difficulty, as discussed in Section 3.0 for iron.

Inadequate fluidity may be overcome by adding more boric to the slag. However this should be considered an interim measure until the furnace can be modified to operate at greater temperatures.

Excessive temperatures, increases the reactivity of the graphite in the crucible, accelerating its destruction and can also cause undesirable reduction of metal oxides from the slag, causing them to be taken up into doré.

The mould is conveniently treated by oiling by a silicon spray (as used for domestic non-stick frying) prior to pouring. Alternatively a smoky acetylene flame can be used to apply a film of soot for promoting good doré separation from the mould. Lime and similar washes can also be applied by brush. The washes must be dried, and the mould preheated prior to pouring the melt. Merely moderate preheating of the mould (e.g. by placement on the furnace) is desired, otherwise spitting occurs during the pour. Furthermore very hot moulds can lead to welding of the gold to the metal at the pour point.

A rapid pour or long drop, causing turbulence is undesirable as this will tend to create shot which may not disengage timeously from a viscous slag. This is particularly so if the slag is too fluid. A temperature giving the consistency of honey is more desirable.

Attempts to incorporate fluorine in the fluxes, revealed in this monograph, in order to reduce slag viscosity have not been very successful. It is suspected that the introduction of fluorine into borosilicate melts has led to the loss of both boron and fluorine (by the formation and volatilisation of BF)

Furthermore it is suspected that fluorine promotes the destruction of the fire clay matrix holding the graphite in the crucible wall through the formation of SiF_6, and through the associated mechanical erosion resulting from localised bubbling resulting from the formation of gas at the crucible wall.

It would also appear that excessive fluorine affects the separation of bullion from the slag by causing a fine gold emulsion to be stabilised in the slag layer adjacent to the doré, which does not separate out prior to solidification.

It is probably of use to record that the substitution of $NaNO_3$ by KNO_3 (motivated by the ready availability of the latter as an agricultural fertiliser, and reports that it is more stable thermally and thus possibly reduce loss of oxidising potential during heating), was a failure. The resulting slag was too viscous.

Soda ash has also not proved to be a very satisfactory flux constituent. The CO_2 released during the smelt has led to foaming and also tends to maintain iron in the ferrous state which is not as readily fluxed as ferric iron.

Some colloidal refractory (high melting point) oxides, if accidentally carried through at the cathodes due to poor processing practices, can cause doré to form a stable emulsion in the slag(See Figure 5) These oxides are often magnetic and can be so separated from concentrates prior to smelting.

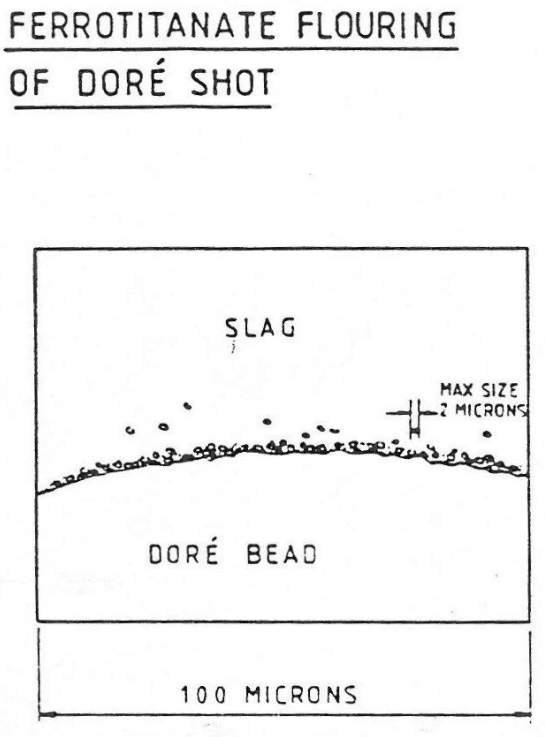


Figure 5. Doré Flouring

Gold emulsions can also be stabilised in the slag by pre-calcination of the steel wool, which introduces a vast amount of high melting point oxides which is not generally taken into the slag.

If the slag tends to creep up the crucible walls, substances such as borax have reduced the surface tension excessively.

Continuing the melt longer than needed should be avoided as this merely increases crucible wear.

Trainor (1986) records a number of useful operating hints, warning on the hygroscopicity of soda in flux, its strong exothermic reaction with water and aggressive attack on skin etc, and noting that charcoal may be used to reduce heavy copper oxide skins by reduction in order to simplify sampling. He also warns on the significant co-transportation of gold with copper oxide into slag when high copper levels exist.

11.0 The Preferred Kiln, Crucible And Heat Source.

The cheapest and most easy to use kiln is probably the fixed type with a swing away refractory cover as well as hood. This gives rapid access for sight and paddling by swinging away the hood and to the crucible by swinging away the cover.

Where a mercury hazard exists, the hood should not be removed until there is negligible risk of further mercury distillation. A powerful toroidal exhaust may also be provided to draw off all exhaust fumes even with the hood off.

The crucible is most comfortably removed using a suspended friction clamp, which may be swung around to the mould. This allows the crucible lip to be held right down to the mould for the most gentle (and least shot-producing) pour, with gentle sideways movement to avoid pouring on one spot.

Any choice between ordinary clay/graphite and silicon carbide bonded clay/graphite crucibles generally lead to a self fulfilling prophecy in that the rejected approach can be demonstrated to be worse in an installed system. Once having selected and successfully installed a system handling one alternative, it cannot accommodate the other well since;

- The greater thickness and the higher thermal resistance of ordinary clay/graphite crucibles necessitates higher flame temperatures for reasonable smelting times. Oil firing which applies a high temperature flame with a high radiant component is not only well suited, but essential for rapid smelting in ordinary clay/graphite crucibles.
- Silicon carbon bonded clay/graphite crucibles have an upper operating temperature of about 1330^{o}C, but are thinner than the ordinary clay/graphite type and are also better conductors of heat. Thus lower flame temperatures are needed during operation, but are also adequate for achieving reasonable smelting times. A gas flame (which is limited to 1300^{o}C) is ideal for these crucibles, whereas the excessive radiant heat component and temperature of oil derived flames would greatly reduce the life of these crucibles.

Since the above indicates that once selected a firing fuel is locked to one type of crucible and vice versa, it becomes necessary to attempt to determine which of the two routes is fundamentally most attractive.

This is surprisingly logical and easy. Doré melts under 1062^{o}C which is comfortably within the 1300^{o}C limit of silicon carbon bonded clay/graphite refractories. There is thus no fundamental objection to reaping the advantages of the lower thermal stress on refractories and reduced loss of heat associated with the lower temperature smelting inherent in applying gas fired heating of silicon carbon bonded clay/graphite crucibles.

Furthermore, the silicon carbide clay/graphite refractory is generally more resistant to slag attack, particularly so at the lower temperatures at which such a system needs to operate. The life of any insulating refractories used for constructing the kiln is also enhanced at the lower temperature and the absence of radiant heat input inherent in gas flames.

Radiant or inductive electric heating may be readily applied for smelting in either type of crucible, but is generally far more expensive than fuel energy.

On the basis of the above a gas fired furnace and a silicon carbon bonded clay/graphite crucible is recommended. Apart from the advantages outlined above, this approach will reduce the consumption of fuel and also the heat stress on operators and exhaust systems.

To further improve crucible life, an internal chrome-magnesia wash (e.g. “J-coat”) will protect against any excessive basicity of desirably fluid fluxes, while an external zircon wash will protect against high temperature attack (by melting) normally particularly prevalent as a result of borax spills. The chrome-magnesia wash will also afford some protection against oxidative attack. Such washes are particularly recommended for carbon containing crucible walls which are not only susceptible to oxidative attack, but which also tend to reduce and deposit iron and base metals. Unfortunately these washes are not commercially available.

The number of a crucible generally denotes the mass of molten brass in kg it can safely contain (the top third is generally left as freeboard). Unless briquetting is resorted to, the crucible capacity to use for Y kg of steel wool is 50 Y kg brass. With briquetting this can be reduced three fold to 17Y kg brass.

The thinner silicon carbide bonded graphite crucibles take less fuel to bring them to temperature and are less liable to failure from stress particularly if operated within their upper operating temperature limit of 1200^{o}C. (1300^{o}C may be applied to clay silica crucibles) The risk of stress failure may be further reduced by keeping a ½ to 2 month inventory of crucibles, after which period the effect of residual manufacturing stresses is reduced. Some extra care in annealing the crucible prior to the first melt is also warranted. In this step the initial heating at 100-150^{o}C to eliminate water is most critical and slow. *Note drying can often be carried out overnight in sample drying ovens common on most mine sites.

12.0 Preferred Insulating Refractories.

The base barrier to undesired loss of furnace heat should be a good refractory of low thermal conductivity and density such as the Babcox & Woolcox MPK 26™ brick. In particular, to accommodate degradation resulting from flux spills, it is desirable to cover this brick with a consumable fibre lining such as B&W Unifelt™

To enhance lining life, it is useful to further coat the lining with a protective zircon wash as discussed earlier, and to regularly inspect the refractory and renovate with cast refractory, fibre and wash such surfaces as have degraded.

In the design of the furnace, it is furthermore obviously desirable to use plinths, clearances and surficial orientations to minimise direct flame impingement particularly on the crucible but also on the kiln structure, and to maximise the input of radiant, conductive and convective heat within the stress limits of the crucible.

At present, designs approaching these ideals are locally offered by Kleenheat (for small melt volumes and manual crucible operation) and also by Furnace Industries (for substantial melt volumes and gentle tilt operation of the bullion pour).

Acknowledgments

The valuable contribution of :

- Ken Baxter, formerly of Hickey Gold Mines and Edward L Bateman Pty Ltd. (now Boddington Gold Mine)
- Bob Carey, of Kleenheat
- Dale Fanning, of Todd Corporation
- Ian Henderson and Ron Jacquet, of Morganite

To this monograph are gratefully acknowledged.

Morganite Crucible Ltd issue a pamphlet (first printed Nov. 1981) which provides an excellent summary of all that constitutes good general practice in the firing of furnaces and the handling of crucibles.

References

1. Barcza N.C. (1985) Director, Mintek. Personal communication
2. Bowen N.J., Shairer J.F. & Willems H.W.V. (1930) The ternary system Na_2SiO_3-Fe_2O_3-SiO_2. American Journal of Science, 5^{th} Series Vol 20, p. 405.
3. Bugbee E.E. (1940) A textbook of fire assaying. Colorado School of Mines Press. Golden, Colorado, (Third Edition). p. 15,155,162,163,180
4. Coudurier L., Hopkins D.W., & Wilkomersky (1978) Fundamentals of metallurgical processes. Oxford, Pergamon Press p. 183-216
5. Elliot J.F. (1984) Slags for metallurgical processes, out of: Fine H.A. & Gaskell D.R. (Eds). 1984 Second international symposium on metallurgical slags and fluxes. The New York Metallurgical Society of AIME, p 45-62
6. Grimshaw R.W. (1971) The chemistry and physics of clays and allied ceramic materials. Ernest Benn Ltd. London p 345-347
7. Hinds H.L. & Trautman L.L. (1983) Refining of precious metal cathodes. Mining Engineering (Nov) p 1545
8. Laatsch H.L. (1925) Die Edelmetalle. Verlag Julius Springer, Berlin. P 69
9. Levin E.M., Robbins C.R. & McMurdie H.F. (1964) Phase diagrams for ceramists. Ohio, The American Ceramic Society
10. Paul. R.L. (1986) The treatment of steel wool cathodes. Lecture 27, The South African Institute of Mining and Metallurgy Carbon School, 8-12 Sept. MINTEK, Randburg, South Africa