

BATH- AND LIQUIDUS TEMPERATURE SENSOR FOR MOLTEN SALTS

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Abstract

A newly developed sensor that measures both bath and liquidus temperature is described. The difference between bath and liquidus temperature is known as superheat. Determination of the liquidus temperature is based on interpretation of the time-temperature trace during cooling down of a sample taken from the bath. Supercooling is avoided by vibrating the sample.

Accuracy and reproducibility of the sensor are discussed. Examples of measurements and series of measurements in point-feed and centre-worked cells are given.

Evolution of bath and liquidus temperature is shown, with respect to feed strategies.

A major conclusion is that to get better information out of temperature measurements, samples taken, or liquidus measurements performed, it is necessary to relate it to timing of the feed strategy in use. Whether analysing bath samples can be replaced by superheat measurements for cell control purposes will be determined by further experimentation.

Introduction

Bath temperature and liquidus temperature are important parameters with respect to the control of an electrolytic aluminium reduction cell because their evolution reflects the thermal balance (1). The liquidus temperature gives information on bath composition (2). Bath temperature and even more, the difference between bath and liquidus temperature (i.e. superheat) determines current efficiency (3); too high a superheat leads to a decrease of current efficiency.

Although a lower superheat results in higher current efficiency, lowering superheat decreases alumina solubility and alumina solution rates (4). This may lead to sludge formation, resulting in horizontal current components in the metal pad. The interaction of these current components with the magnetic field results in an unstable metal pad (5), (6).

Operating the cell at superheats too low may also lead to instabilities because of metal rolling. The density difference between bath and metal decreases with decreasing temperature (7). Running a cell at too high a temperature also means that too much energy is wasted as thermal losses (1) and anode carbon consumption increases (8). Whether bath temperature may decrease depends more on superheat than on bath temperature itself.

If thermal cycling of the bath is reduced, thermal cycling of the cathode blocks is also reduced (9). Better control of superheat leads to more stable ledges (1). This may result in an increased cell lifetime.

Present situation

These days, bath temperature is commonly measured with type K mineral insulated metal sheathed thermocouples (10). Liquidus temperature is calculated out of chemical analysis data (2). However, both methods suffer from certain drawbacks.

Temperature measurement.

- Inherently the accuracy of type K thermocouples is inferior to the accuracy of type S thermocouples. To some degree this problem can be overcome with the application of tedious calibration procedures, but it always will be difficult to deal with the drifting of the signal.
- The metal tubing is a good heat conductor but heat transferred to the sensor is limited and controlled by convection rates, immersion depths and superheat. A dynamic equilibrium will be established depending on how and where the sensor is immersed.
- The measurement is somewhat operator dependent. Because of the long response time, the signal will increase only very slowly near thermal equilibrium and it is difficult to judge when bath temperature is reached.

Calculation of liquidus temperature.

- Recently published equations that relate liquidus temperature with bath composition give results that differ only slightly (2) in the composition ranges used in industrial baths. We can assume that these equations are accurate enough to be used in practice. Moreover, any error would be a systematic one, and has no consequence on cell control. However, in order to be able to calculate liquidus temperature from analysis data, it is of course necessary to know the concentration of all influencing components. This is not always the case (e.g. alumina, impurities).
- Errors in analytical data will result in erroneous liquidus data.

Errors in both bath and liquidus temperature will accumulate when superheat is calculated. The aim of obtaining more accurate bath- and liquidus temperatures - and hence superheat - led to the development of a new sensor that measures them both - at the same time.

Measurement principle and design of the sensor.

Figure 1 shows the design of the sensor.

The method is based on the principle of thermal analysis. A sample of bath is taken in a metal cup (#4 from figure 1) and cooled down. When the liquidus temperature (primary freezing point) is reached, heat of fusion is released and the rate of cooling is decreased. Out of the time-temperature trace, the inflection point that corresponds with the primary freezing point, can be calculated.

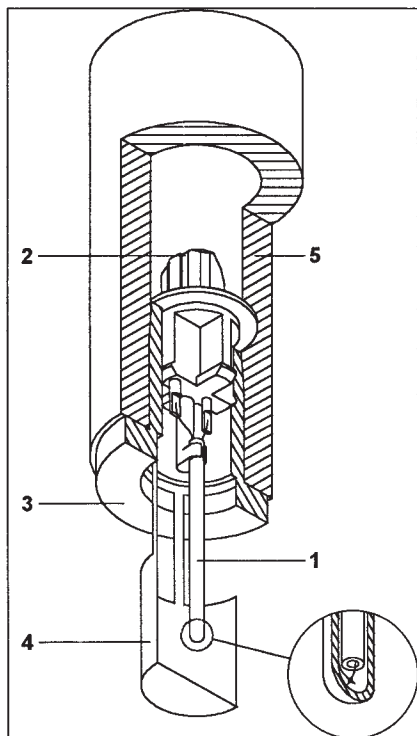


Figure 1: Design of the sensor

In principle, the method is very simple, but several precautions have to be taken in order to obtain the correct liquidus temperature. A well-known problem with this kind of measurement is the phenomenon of supercooling, e.g. the cooling below the liquidus temperature without the formation of any solid phase. At higher cooling rates, this problem is more likely to occur (11).

The problem can be overcome in two ways.

1. The inner surface of the cup (#4) that contains the bath sample is roughened by means of sandblasting to provide many active sites on which nucleation of the solid phase can start.
2. During cooling down the sample is vibrated. Typical vibration characteristics are: frequency between 200 and 400 Hz and amplitude about 0.1 mm.

The effect of the release of heat of fusion during cooling through the liquidus point can be obscured if the total thermal mass of the materials in contact with the bath sample is too high. This leads to badly defined inflection points (rounding of the otherwise quite sharp break in the time-temperature trace). Wall thickness of the copper cup (#4) is minimised ($\leq .1$ mm) and the diameter of the quartz tube (#1) which contains the thermocouple is small (≤ 1.7 mm).

Quartz is of course attacked by liquid cryolite and this has to be avoided for two reasons:

1. When cryolite reaches the thermocouple wires, temperature readings become useless.
2. Silica contamination of the bath sample will lower its liquidus temperature.

The quartz tubes are protected against corrosion by means of a thin molybdenum and/or copper coating.

The cavity of the ceramic body (#3) is filled with high alumina refractory cement. The plastic connector (#3) holds the electrical contacts in place.

Before the sensor is withdrawn from the cell, it comes to thermal equilibrium with the bath and bath temperature is read. Because of the low thermal mass this happens within 15 to 20 seconds, so the measurement is operator independent. However, the sensor has to stay for about 30 seconds in the bath to make sure all bath that solidified around the cup is remelted. Immersion depth is about 5 to 10 cm. After withdrawal the cup (#4) and sample of bath contained therein are allowed to air-cool.

As mentioned earlier, the tubing of the sensor can disturb the thermal equilibrium of the direct surroundings of the sensor. To avoid this, we make use of cardboard tubes (#5), that have very low heat conductivity.

Figure 2 gives two examples of measurements in 150 kA centre worked half breaker cells with prebaked anodes. The first gives a bath temperature of 962.5 °C and a liquidus temperature of 949.4 °C; the second gives 970.8 °C and 967.7 °C, respectively.

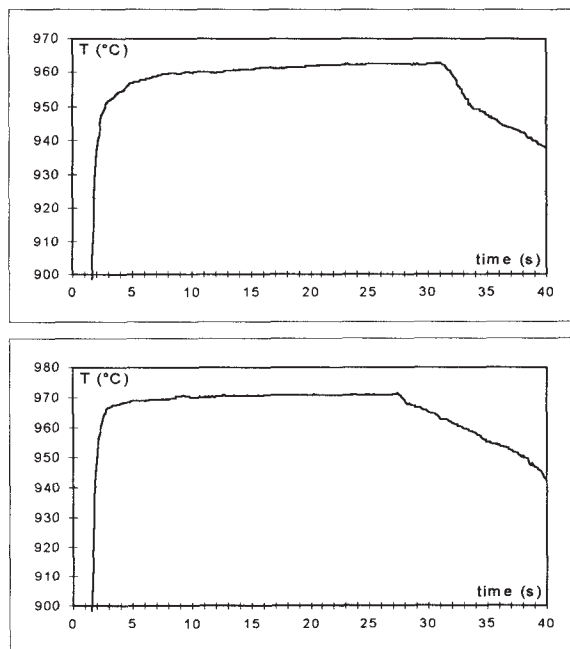


Figure 2: bath- and liquidus temperature measurements in 150 kA centre worked cells with half bar breakers

Calibration

It's only possible to obtain a high accuracy if one starts from an accurate thermocouple. This is why we do not use type K thermocouples but prefer type S (Pt-Pt10%Rh, IPTS 68). Calibration of the wires is done against the melting point of gold. The accuracy is 1064 ± 0.5 °C.

Because other structural elements of the sensor also can affect trace quality or accuracy, the behaviour of the sensor is also checked in "standard" melts. For this purpose we use molten NaCl. (About 5 kg of NaCl are melted in a graphite crucible, suspended in an induction furnace.) An example of a trace obtained in molten NaCl is given in figure 3.

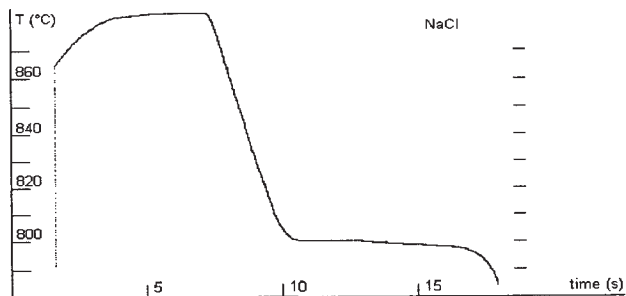


Figure 3: Time-temperature trace in molten NaCl

Experimental data

All measurements were performed in 150 kA cells with prebaked anodes. Centre worked cells with half bar breakers are designated CWPB in the following text and figures. Cells with point feeders are designated PF.

Reproducibility tests

First, examples of series of measurements in CWPB cells are given. Since addition of alumina affects both bath and liquidus temperature, measuring started some time after a crust break / feed action ; once the bath and liquidus temperature has stabilised.

Figures 4 and 5 show the evolution of bath and liquidus temperature and superheat in cells with low superheat; figures 6 and 7 cover cells with high superheat.

From this and other studies measurements are more reproducible at lower superheats.

Figures 8 and 9 show bath and liquidus temperature measurements and the evolution of superheat in PF cells. Again it is clear that the lower the superheat, the more reproducible the measurements are.

Influence of feed cycles in centre worked cells

The influence of feed cycles on the evolution of bath and liquidus temperature and superheat is given in figures 10 and 11. The vertical lines indicate a crust break / feed action. An A-break is a break at the duct end of the cell; a B-break is a break at the tap end. All the measurements of bath and liquidus temperature were carried out at the duct end of the cells.

After a crust break and feed action at the same side as where the measurements are made (A-break), bath and liquidus temperature both drop immediately. Also superheat drops, so bath temperature decreases more than liquidus temperature.

When the break / feed action takes place at the opposite side from where the measurements are taken (B-break) a sudden increase in liquidus temperature is observed most of the time. This was also observed on other cells and is a phenomenon which can not be explained.

Influence of feed cycles in point feed cells

The influence of different feed cycles (i.e. base feeding, accelerated feeding and no feeding) is shown in figures 12 and 13. The first gives the evolution of bath and liquidus temperature. The second gives superheat.

The last no feeding period lasted until an anode effect occurred.

During accelerated feeding both bath and liquidus temperature go down; during a no feeding cycle they go up.

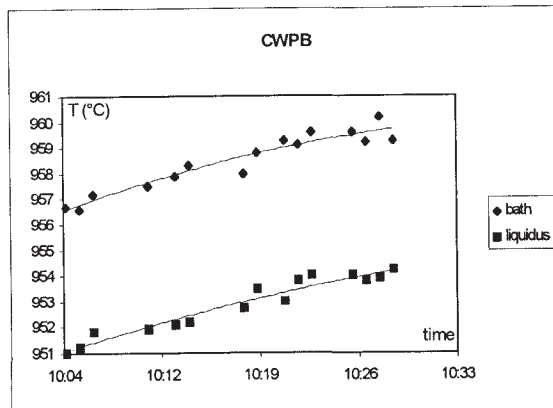


Figure 4: Measurements in CWPB cells: low superheat

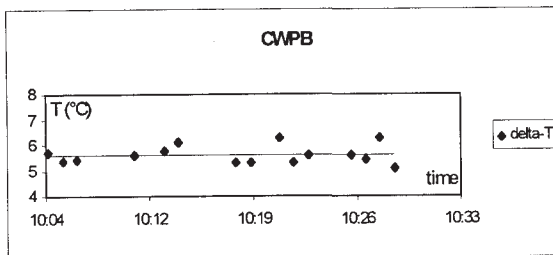


Figure 5: Reproducibility of superheat in CWPB cells: low superheat

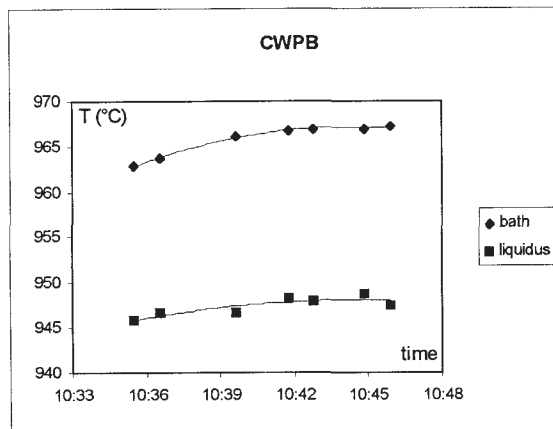


Figure 6: Measurements in CWPB cells: high superheat

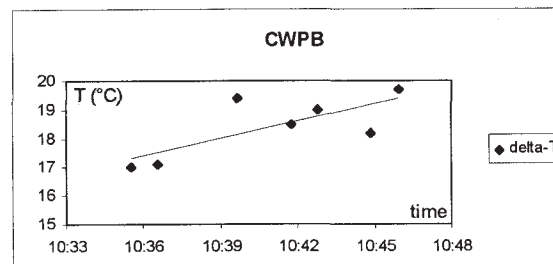


Figure 7: Reproducibility of superheat in CWPB cells: high superheat

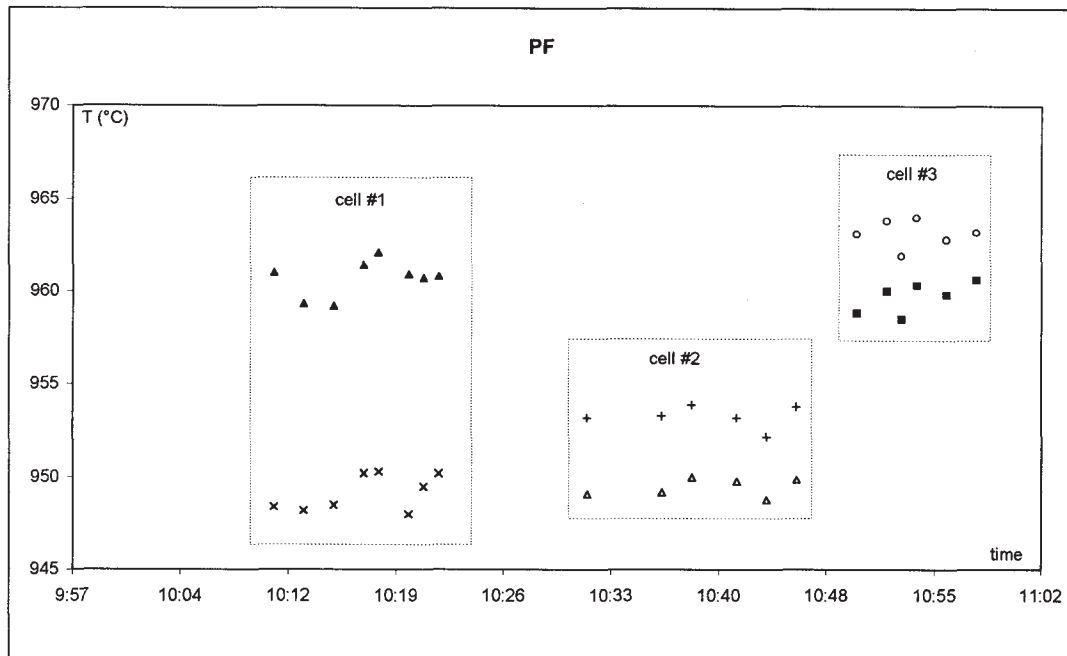


Figure 8: Bath- and liquidus temperature in point feed cells. Bath and liquidus temperatures of different cells are given on the same time-temperature graph

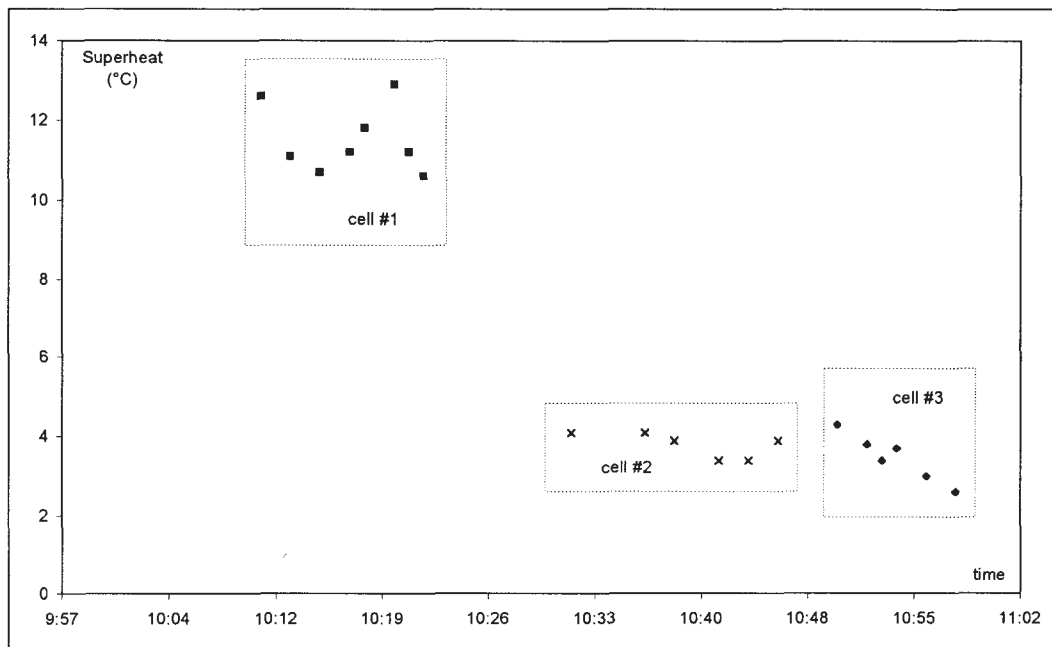


Figure 9: Evolution of superheat in point feed cells described in figure 8

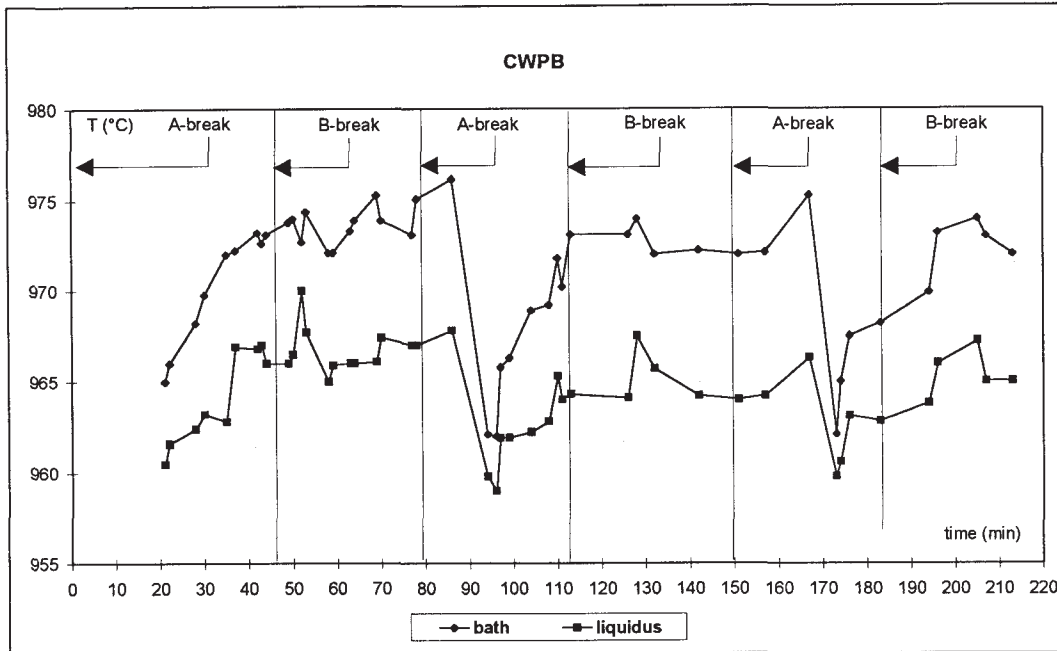


Figure 10: Evolution of bath and liquidus temperature in CWPB cells with respect to feed cycles

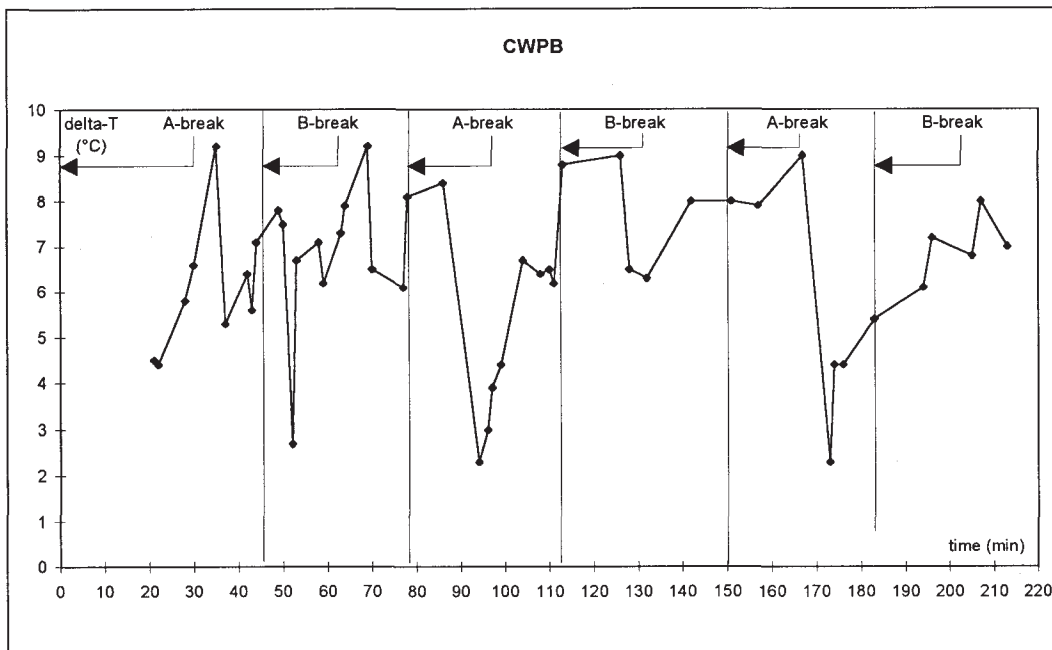


Figure 11: Evolution of superheat in CWPB-cells with respect to feed cycle

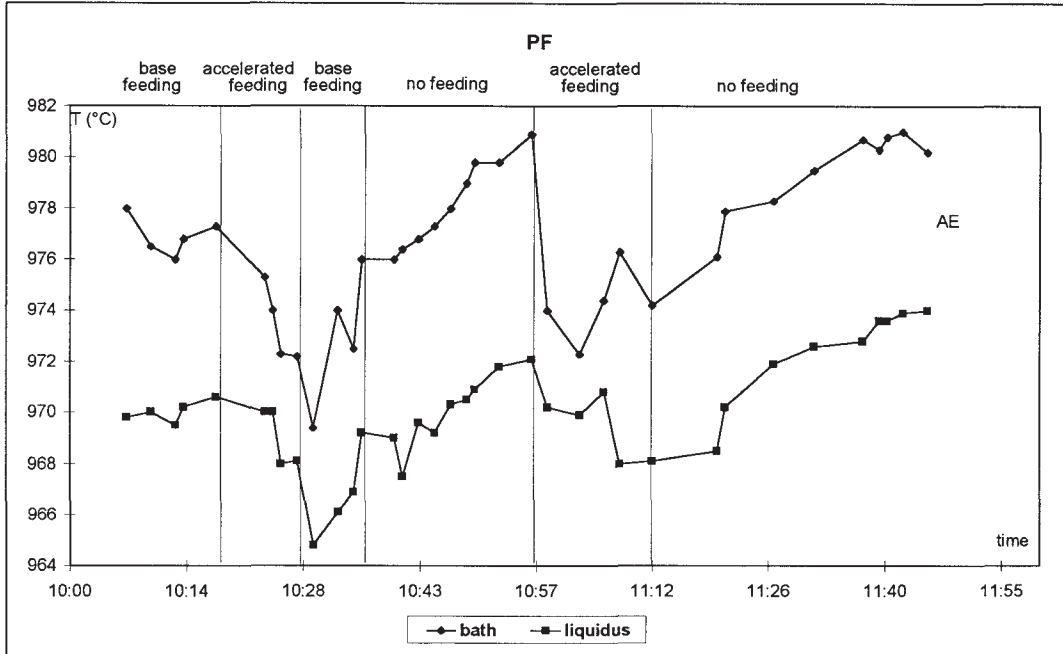


Figure 12 : Influence of feeding on bath and liquidus temperature in point feed cells

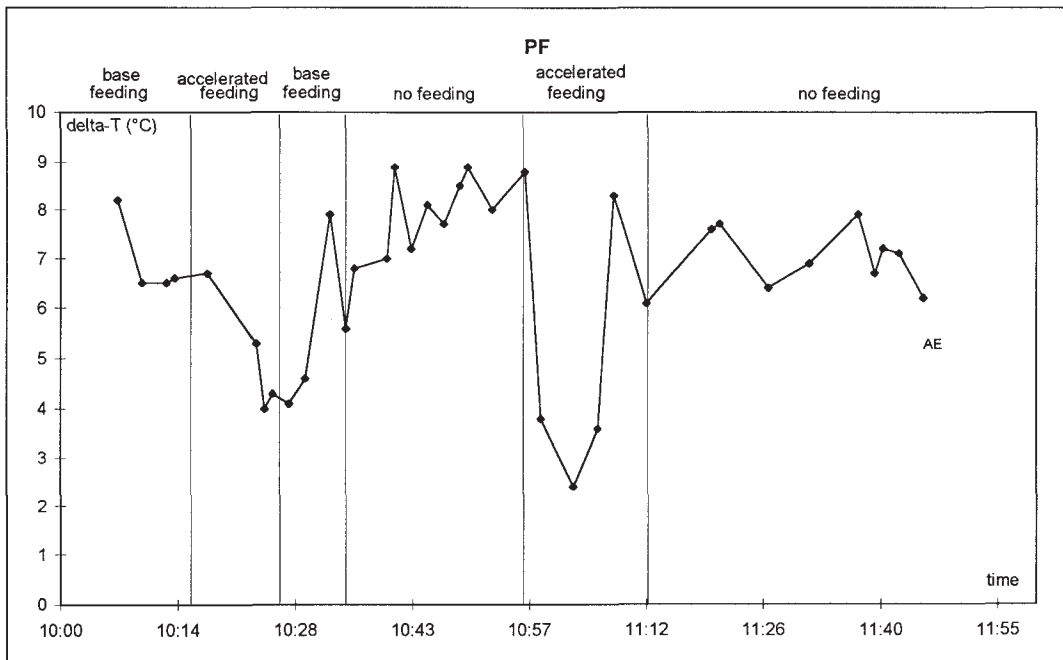


Figure 13 : Influence of feeding on superheat in point feed cells

The measurements are much more consistent when taken during a no feeding period. During feeding - at base or accelerated rates - there are larger fluctuations.

Even the quality of the individual measurements is affected by feed actions. Normally when the sensor comes to thermal equilibrium with the bath, the signal is very steady (figure 2). When measurements are taken during feeding in PF cells swings on the temperature signal of a few degrees C can be observed.

Discussion

Trace shape

Temperature-time-trace shapes obtained in molten NaCl differ from those obtained in molten cryolite. In NaCl, when the melt is solidifying, temperature stays constant for a period of time and in liquid bath there is only an inflection at the liquidus temperature. Figure 14 reflects these trace shapes in a schematic way.

This is in agreement with Gibbs' phase rule (11). When a pure component solidifies, two phases with the same composition coexist and temperature at this invariant point stays constant until all of the liquid phase solidified. Solidification of a mixture of components involves a change of composition of the coexisting phases. Formation of more solid phase requires a decrease of temperature, so no flat is observed in the time-temperature trace, except at other invariant points, e.g. a eutectic.

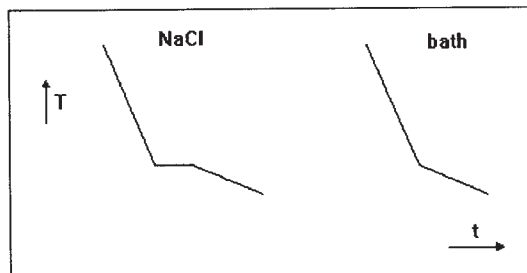


Figure 14: time-temperature traces for pure components and mixtures

Supercooling

Supercooling is a very well known phenomenon to users of thermal analysis. The normal technique to avoid supercooling is to have the melt cooled down very slowly (11).

The use of the sensor described, involves fast, natural cooling of the small sample taken from the bath. Without any precautions taken, liquidus temperature determination would suffer from an irreproducible amount of supercooling, making the sensor useless.

Researchers who studied the phase diagram or liquidus temperature equations of cryolitic melts encountered the same problem. They overcame the problem first, by applying slow cooling, and second, by stirring the melt and adding seeds, e.g. (2) and (12).

The same principles, apart from slow cooling, were applied to the sensor.

Instead of adding seeds - that provide nucleation sites for the solid phase to be formed - the inner surface of the cup that contains the bath sample is sandblasted. Since the first solidification indeed takes place on the outer parts of the sample, this is where nucleation has to be triggered. Stirring of the melt is replaced with vibrating the sample at high frequencies. This turned out to be very effective, so the fast cooling rates are no longer a problem.

Influence of feed cycles

Since liquidus temperature depends on alumina concentration and bath temperature drops when alumina is added, the response of the sensor will depend on the feed cycles in use. This became clear from the examples given for both centre worked and point feed cells.

Although in point feed cells alumina concentration is rather constant over a long period of time, on a smaller time scale fluctuations, inherent to the process do exist. For this reason measurements are not as reproducible as they are in centre worked cells some time after a crust break / feed action. However, if feeding is interrupted for some time, consistent measurements can be made in PF cells. It is possibly a good strategy, if the sensor is used for cell control, to deliberately interrupt the feed cycle some time before measuring and afterwards increase the feed rate for some time to make up for the difference.

In centre worked cells it is better not to measure immediately after feeding. If feeding occurs at the same side as where the measurements are taken, bath and liquidus temperature drop sharply. If feeding occurs at the other side, most of the time liquidus temperature goes up, a phenomenon we can not explain yet.

Because liquidus temperature is changing with feed actions, it is necessary to include information on timing relative to the feed schedule, in the data obtained.

Since liquidus temperature reflects bath composition, we can conclude the same for samples taken at different times with respect to the feed cycles in use.

If superheat is to be calculated, timing is even more important.

Superheat calculations need bath temperature that is measured with a thermocouple, and liquidus temperature that is calculated from the composition of a sample, or measured with a sensor. When a sensor is used, bath and liquidus temperature are measured at the same time and calculated superheat is the superheat at that time. When a sample is used to determine liquidus temperature, the sample should be taken at the same time temperature is measured. Neglecting this will yield erroneous superheat data.

From figures 10 and 12 it follows that on a rather short time span maximum liquidus temperature can be higher than minimum bath temperature. If timing of both determinations is not respected, this can lead to the conclusion that cells are running at a negative superheat. These observations might help in explaining the so called "liquidus enigma", as described by W. Haupin in (13).

Metal rolling

When metal rolling occurs, the cups that contain the bath sample are perforated because of alloying of the copper with aluminium droplets, as shown in figure 15. Obviously no liquidus temperature measurements can be made with the sensor during metal rolling, since the liquid bath sample will flow out through the perforations.

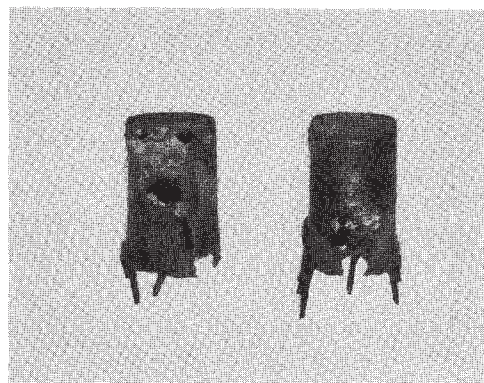


Figure 15 : Cups perforated by metal droplets

It happened that a cell was behaving normal and liquidus temperature measurements were performed. A crust break / feed action took place and a few minutes later the metal rolling started. From then on all of the cups were damaged by aluminium alloying. Possibly the crust break / feed action triggered the phenomenon. Cell conditions at this time were: 953,5 and 947 for bath and liquidus temperature.

Future developments

Whether superheat measurements can be used for cell control purposes will be determined by further experimentation. The way sensor output can be used will probably differ from smelter to smelter, depending on the control strategies in use.

Conclusions

- A sensor that measures bath and liquidus temperature in molten salt bath at the same time has been developed.
- Feed strategies influence bath and liquidus temperature. When these parameters are measured, it is important to measure their timing relative to feed actions.
- In CWPB cells it is recommended not to measure immediately after feeding.
- To determine the superheat of a bath, bath temperature measurement and sampling of the bath to determine liquidus temperature, or liquidus temperature measurement with a sensor should be carried out at the same time and the same location.

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