SUPERHEAT SENSOR FOR ELECTROLYTIC HALL-HÉROULT CELLS

Paul Verstreken

Heraeus Electro-Nite Int. N.V.
Centrum-Zuid 1105
3530 Houthalen
Belgium
Phone : +32 11 60.02.11

ABSTRACT

The industrial application of an immersion sensor for measuring bath and liquidus temperature in molten cryolite baths is described. The resulting superheat reflects the thermal situation of the electrolytic cell. The on-line availability of these data may lead to better process control during primary aluminium production.

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, 14). 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, it may not be too low because of decreased 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, 13).

Operating the cell at too low superheats may also lead to instabilities because of metal rolling. The density difference between bath and metal decreases with decreasing temperature (6).

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 (7). 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 (8). Better control of superheat and bath temperature leads to more stable ledges (1, 14). Ledge formation and dissolution are controlled by superheat and ledge melting is controlled by bath temperature (14). 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 (9). Liquidus temperature is calculated out of chemical analysis data (2). However, both methods suffer from certain drawbacks.

1. 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, when performing consecutive measurements.
- 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 thermal E.M.F. will increase only very slowly near thermal equilibrium and it is difficult to judge when bath temperature is reached.

2. 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 on analysis data will result in erroneous liquidus data.

Errors on 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. The calculation is based on looking for the relevant maximum of the second derivative.
In principle, the method if very simple, but several precautions have to be taken in order to read the correct liquidus temperature. A well-known problem with this kind of measurements 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 (10).
We overcame this problem 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 at a frequency of about 280 Hz and an amplitude of 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 (≤ .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 copper coating.

The cavity of the ceramic body (#3) is filled with high alumina refractory cement. A plastic connector (#2) 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 ... 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 ... 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.

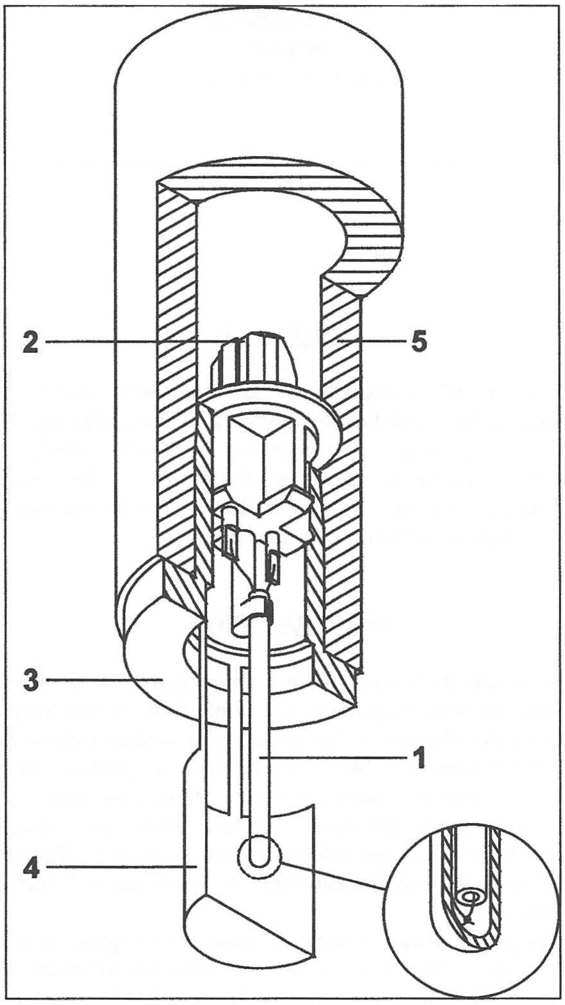

Figure 1: Design of the sensor

Figure 2 shows a typical example of four consecutive measurements in a 150 kA centre worked half breaker cell with prebaked anodes. Bath and liquidus temperature and superheat, as calculated by the measuring and interpretation unit, are shown in table I.

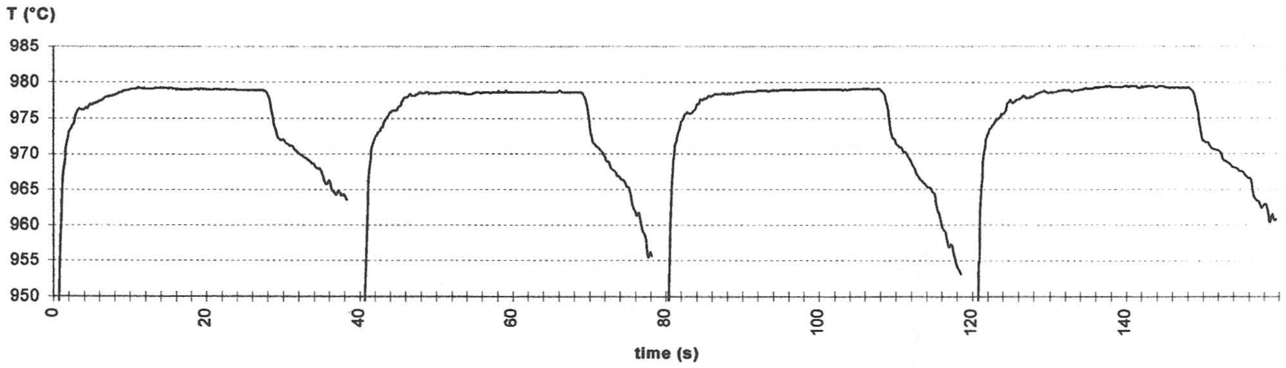

Figure 2: Consecutive bath- and liquidus temperature measurements in a 150 kA centre worked cell with half bar breakers

Table I: Interpretation of the measurements from figure 2

	Bath temperature	Liquidus temperature	Superheat
	(°C)	(°C)	(°C)
1	978.9	972.2	6.7
2	978.6	971.8	6.8
3	979.1	972.2	6.9
4	979.2	972.4	6.8

Calibration

It is 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.

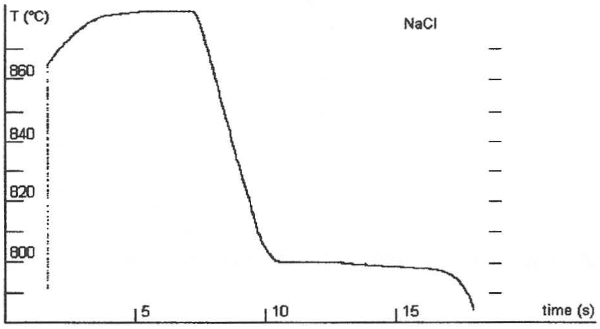

Figure 3: Time-temperature trace in molten NaCl

Reproducibility

From table I it follows already that a good reproducibility in both bath and liquidus temperature measurement, and hence superheat determination, is obtained. The reproducibility of the sensor is discussed in more detail in (15). It follows that at lower superheats a better reproducibility is obtained.

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 figure 4. Figure 5 represents the evolution of superheat. The vertical lines indicate an action of the breaker bars.

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.

DISCUSSION

1. 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 (10).
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.

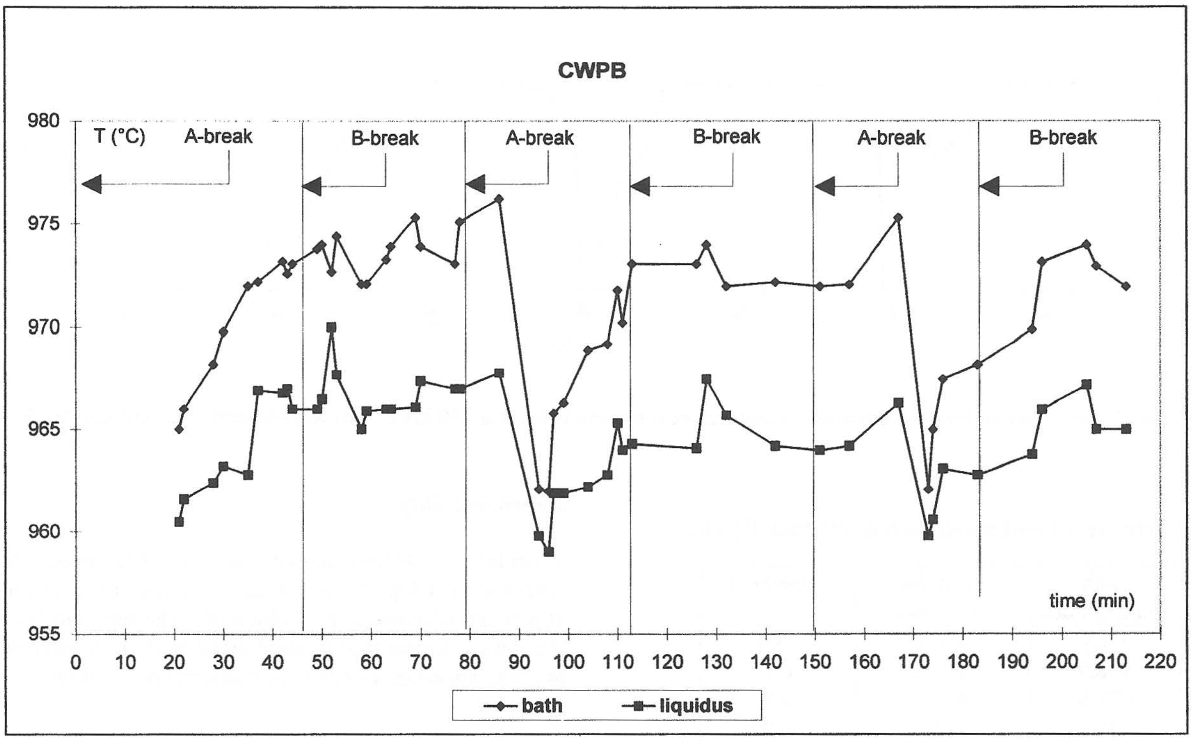

Figure 4: Evolution of bath and liquidus temperature in CWPB cells with respect to feed cycles (15)

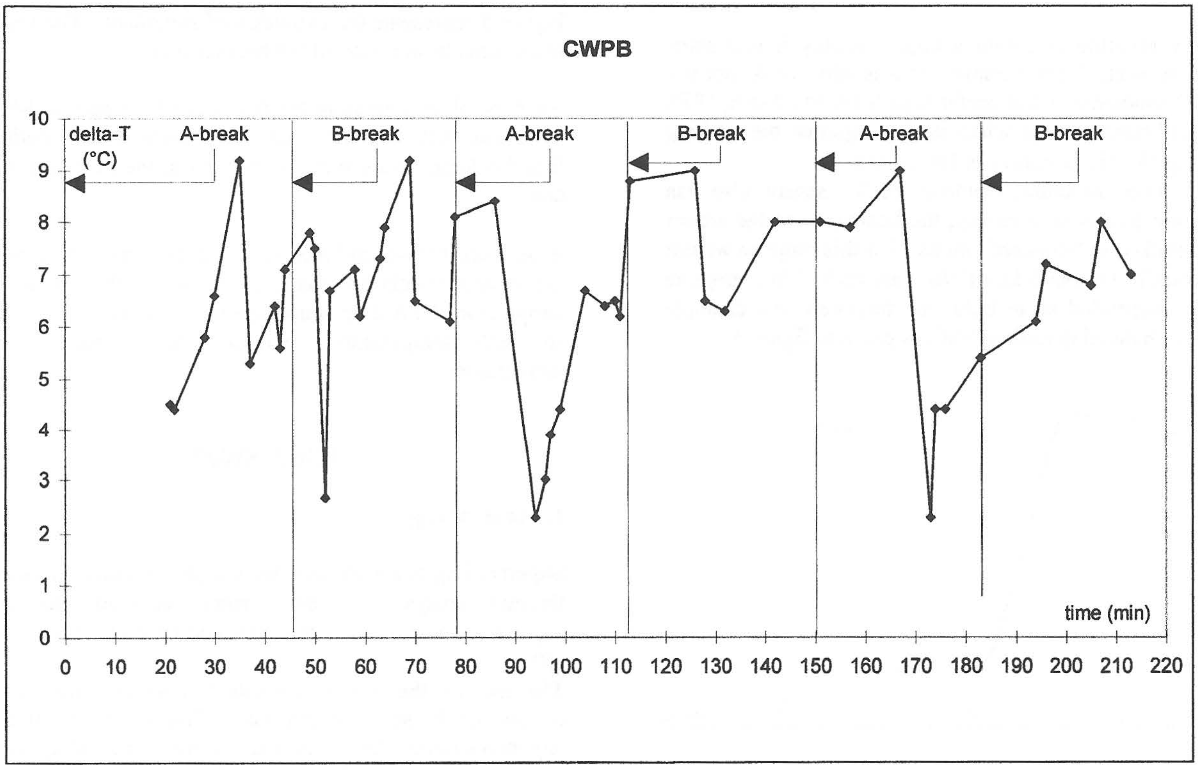

Figure 5: Evolution of superheat in CWPB-cells with respect to feed cycle (15)

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 (11).
The same principles, except 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 faster cooling rates are no longer a problem.

2. 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.
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. This temperature drop, and also the time to recover, increase when a corner anode is freshly set.
Although in point feed cells alumina concentration is rather constant in a long period of time, on a smaller time scale up and down fluctuations, inherent to the process, do exist.
In both systems - bar breakers and point feeders - liquidus temperature is changing with feed actions. Therefor it is necessary to include information on timing relative to the feed schedule in the data obtained.
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 figure 4 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 (12).
If negative superheats do exist, this sensor is not able to detect them.

3. Metal rolling

When metal rolling occurs, the metal cups are perforated because of alloying of the copper with aluminium droplets. In this case, no liquidus temperature measurements can be made with the sensor, since the liquid sample taken will flow out through the perforations.
Aluminium droplets also may alloy with the copper coating on the quartz, exposing it to cryolite attack.

4. Future developments

Whether superheat measurements can be used for cell control purposes will follow from ongoing experiments.
The way sensor output can be used will probably differ from smelter to smelter, depending on the control strategies in use. Because the liquidus temperature of the bath depends on its total composition, the possibility to determine the concentration of one component, e.g. aluminium fluoride, depends on the accuracy with which the other components are known. As an example, the liquidus temperature as a function of aluminium fluoride is calculated for a bath containing 5 wt% CaF_2 and different alumina concentrations (figure 6). Solheims' equation is used for the calculations (2). The incertitude on the aluminium fluoride concentration is of about the same order of magnitude as the incertitude on the alumina concentration. This incertitude decreases with increasing acidity of the bath.
An interesting question in this respect is how accurate the aluminium fluoride concentration must be known when liquidus temperature no longer has to be calculated from bath composition, but is measured directly.

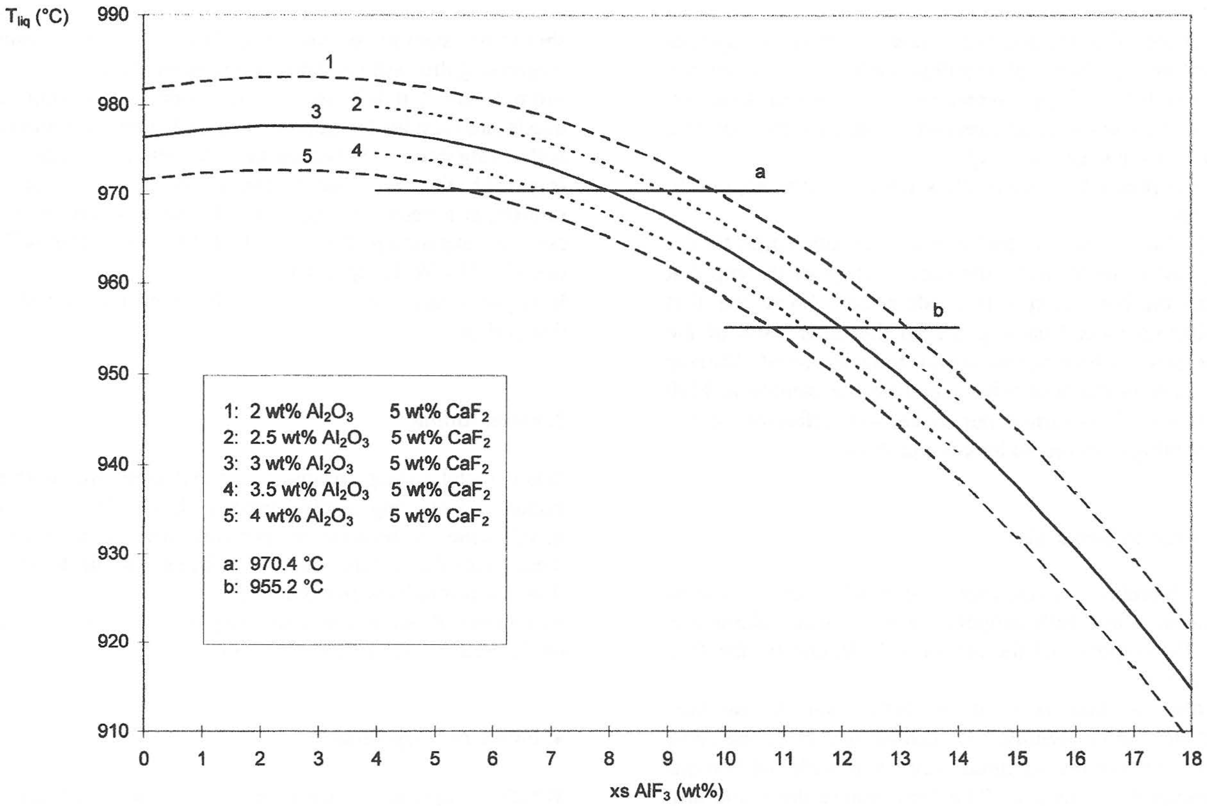

Figure 6: Liquidus temperature as a function of aluminium fluoride concentration for different alumina contents

CONCLUSIONS

- A sensor that measures bath and liquidus temperature at the same time is developed.
- Feed actions influence bath and liquidus temperature. When these parameters are determined, timing relative to feed actions should be known.
- In CWPB cells it is recommended not to measure immediately after feeding.
- To determine superheat, bath temperature measurement and sampling of the bath to determine liquidus temperature, or bath and liquidus temperature measurements with a sensor should be carried out at the same time.

REFERENCES

1. Taylor M.P. "Static and dynamic energy balance in reduction cells", Paper at the International Course on the Process Metallurgy of Aluminium, Trondheim, Norway, May 24-28, 1993

2. Solheim A. et al. "Liquidus temperature and alumina solubility in the system Na_3AlF_6-AlF_3-LiF-CaF_2-MgF_2", Light Metals 1995 p. 451-460

3. Dewing E.W., "Loss of current efficiency in aluminum electrolysis cells", Met. Trans B, 22B, 1991, p. 177-182

4. Kuschel G.I., Welch B.J., "Further studies of alumina dissolution under conditions similar to cell operation", Light Metals 1991 p. 299-305

5. Segatz M., Droste C., "Analysis of magnetohydrodynamic instabilities in aluminum reduction cells", Light Metals 1994 p. 313

6. Utigard T.A., "Density of the Na_3AlF_6-AlF_3-Al_2O_3-CaF_2 system: a key to the performance of Hall-Héroult cells", Light Metals 1993, p 239-245

7. Fischer W.K. et al., "Interdependence between anode net consumption and pot design, pot operating parameters and anode properties", Light Metals 1991, p. 681-686

8. Sørlie M. et al., "Early failure mechanisms in aluminium cell cathodes", Light Metals 1993, p. 299-308

9. Madsen D.J., "Temperature measurement and control in reduction cells", Light Metals 1992, p. 453-456

10. Kipouros G.J., Sadoway D.R., "Molten salts: Fundamentals and industrial applications", Short Course at the TMS Annual Meeting, Las Vegas, Feb 11th, 1995

11. Holm J.L., "The phase diagram of the system Na_3AlF_6-CaF_2 and the constitution of the melt in the system", Acta Chem. Scand. 22, (3), 1968, p. 1004-1012

12. Haupin W., "The liquidus enigma", Light Metals 1992, p. 477-480

13. Urata N., "Magnetics and metal pad instability", Light Metals 1985, p. 581-591

14. Welch B.J., Liu X., "Thermochemistry of electrolyte and cell operation." Paper at the International Course on the Process Metallurgy of Aluminium, Trondheim, Norway, June 3-7, 1996

15. Verstreken P., Benninghoff S., "Bath- and liquidus temperature sensor for molten salts", Light Metals 1996, p. 437-444

For further information on this paper, please contact
Paul Verstreken at Heraeus Electro-Nite International N.V.,
Centrum Zuid 1105, 3530 Houthalen, Belgium
Phone : +32 11 60.02.11
Fax : +32 11 60.04.00