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Test of Dip Cup Instrumentation

B. B. Brenden

November 1988

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Richland, Washington 99352

SUMMARY

Instrumentation has been developed which will measure the alumina content of cryolite baths based upon the detection of a thermal arrest in the cooling curve when a small sample is pulled from the bath using a graphite cup. Detection of the temperature at which thermal arrest occurs is automatic, and an alumina content is automatically calculated and displayed. Recent measurements at a production plant indicate a standard error of 0.38% or less in the determination of alumina content based upon a set of 9 measurements. The time required for a single measurement is less than 5 minutes. No further development of the technique or instrumentation is planned at the present time.

TABLE 1. Summary of Measurement Results

<u>Bath A</u>		<u>Bath B</u>	
Bath Ratio	1.126	Bath Ratio	1.238
CaF ₂	4.8%	CaF ₂	5.08%
Alumina Content by:		Alumina Content by:	
Chemical Analysis	3.34%	Chemical Analysis	3.60%
Dip Cup Instrument	3.29%	Dip Cup Instrument	3.67%

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TEST OF DIP CUP INSTRUMENTATION

BACKGROUND

During the course of work to develop instrumentation to measure the alumina content of cryolite baths, a method has evolved based upon the measurement of the temperature at which a thermal arrest occurs during the cooling of a small sample dipped from the bath using a graphite cup having a volume of about three cubic centimeters. Instrumentation has been developed to facilitate the use of this method. The instrumentation is very compact and portable. It consists of a lightweight handling arm which is used to place the dip cup in the bath and an electronics package housed in a small suitcase measuring 21" x 15" x 7". The electronics package, weighing less than 10 pounds, is battery operated and consists of standard commercial equipment including an HP-3421 Data Acquisition System and an HP-71B hand-held computer. Figure 1 provides a block diagram of the electronics package. Figure 2 is a schematic drawing showing the dip cup immersed in the cryolite bath.

Tests at the Pacific Northwest Laboratory (PNL) using baths of various bath ratios but containing no spar (CaF_2) gave the results shown in Table 2. In Table 2 a quality factor is listed which is calculated and displayed by the computer. This is a measure of how well the transition temperature is detected. Note that two of measurements at 6% alumina had very low quality factors. The data related to the low-quality factors was excluded from the calculation of Mean Values and Standard Deviations. The data indicates excellent repeatability of the transition temperature and its measurement. This translates to excellent repeatability for determination of weight percent alumina. At the time that these measurements were made, the emphasis was upon high alumina content; but it is expected that similar results would be obtained with baths containing less than 6% alumina.

The instrumentation was introduced to the production environment at the Kaiser Aluminum plant at Mead, Washington, on September 22, 1987. Based upon that experience, further improvements were made to prevent melt off of the dip

FIGURE 1. Block Diagram of Electronics System

FIGURE 2. Dip Cup Immersed in Cryolite Bath

cup support, heat damage to the thermocouple connection sockets, and to take into consideration the spar content.

TABLE 2. Data Taken When Using Automated Dip Cup Instrumentation with High Alumina Content Cryolite Bath

<u>Wt. % Alumina</u>	<u>Transition Temperature</u>	<u>Quality Factor</u>	<u>Maximum (Start) Temperature</u>	<u>Mean Transition Temperature *S.D.</u>	<u>Mean* Wt. % Alumina *S.D.</u>
6	941.4	2.1	997.9		
6	945.8	8.2	972.1		
6	901.5	0.4	922.5		
6	944.0	43.8	959.9		
6	901.4	0.0	911.0		
6	942.3	8.6	1006.0		
6	943.4	6.2	1009.0	943.27	6.00 *.17
6	944.1	6.8	979.6	*1.03	
6	943.4	9.1	995.6		
6	942.6	8.1	990.7		
6	942.8	6.1	997.7		
6	943.2	10.8	992.3		
6	943.2	13.3	999.1		
6	943.0	16.5	999.8		
7	938.8	13.8	981.0		
7	939.1	8.0	997.9		
7	938.8	10.8	987.4	939.13	6.67 *.05
7	939.5	7.7	998.0	*0.32	
7	939.6	7.6	991.7		
7	939.0	9.3	984.3		
8	932.7	11.1	982.0		
8	932.6	10.0	985.2	932.6	7.76 +.09
8	932.7	11.9	986.2	*0.58	
8	931.2	8.9	996.1		
8	932.6	6.4	1002.0		
9	925.3	35.0	1003.2		
9	924.6	42.0	990.6		
9	924.9	38.8	985.3	924.70	9.00 *.06
9	924.6	20.6	996.2	*0.37	
9	924.7	6.6	992.9		
9	924.1	12.7	997.7		

*Based upon a linear fit pegged at 6% and 9%.

RECENT TEST RESULTS

A second test of the instrumentation was performed at the Kaiser Mead Plant on August 18, 1988. A series of 18 measurements were made over a time interval of 90 minutes. Thus, a measurement cycle takes on the average of 5 minutes. During this period one thermocouple developed a short and was replaced and one dip cup fell off as a result of the nichrome wire support melting during its fourth insertion into the bath. The replacement of this dip cup was also included in the 90-minute activity. The nichrome wire on the first and the last (third) dip cups did not indicate any weakness or melting even though one was dipped 9 times and the other was dipped 6 times.

The data taken during this second test is shown in Table 3. A total of 8 readings taken in Pot 2 yielded a mean value of 942.3°C for the transition temperature (the temperature at which thermal arrest occurs). The standard deviation for these readings was 3.9°C, and the estimated standard error of the mean is calculated as 1.4°C. Pot 3 had a mean transition temperature of 964.3°C with a standard deviation on individual readings of 6.1°C. The estimated standard error of the mean is 2.0°C. The manner in which these statistical values are calculated is discussed in Appendix A.

The equation used to calculate the percent alumina in the bath is taken from Lee et al. (1984). This equation is

$$\begin{aligned} T(\text{Liquidus})(\text{deg. C}) &= 1009.4 + 4.059(\text{CaF}_2) - 1.167(\text{CaF}_2)^2 \\ &\quad + 0.968(\text{CaF}_2)(\text{AlF}_3) - 0.105(\text{CaF}_2)(\text{AlF}_3)^2 \\ &\quad + 0.073(\text{CaF}_2)^2(\text{AlF}_3) + 0.002(\text{CaF}_2)^2(\text{AlF}_3)^2 \\ &\quad - 4.165(\text{AlF}_3) - 0.054(\text{AlF}_3)^2 - 5.33(\text{Al}_2\text{O}_3) \\ &= 1009.4 + K - 5.33(\text{Al}_2\text{O}_3). \end{aligned} \quad (1)$$

The equation is valid only if the CaF_2 content lies between 3.8% and 11% and the excess AlF_3 content lies between 5% and 20%. The factor 'K' is defined by the equation. It represents all terms other than the first and last.

The transition temperature that is observed using the dip cup is related to the liquidus temperature but may not be identical to it. It is possible that the liquid supercools under the conditions that the measurement is made.

It was observed that the transition temperature, T_t , was given correctly by this equation if the constant 1009.4 is lowered to 1001. Thus, in calculating the alumina content, the following equation was used:

$$\text{Al}_2\text{O}_3 = (1001 + K - T_t)/5.33. \quad (2)$$

The results obtained using this equation are given in Table 3 and are in good agreement with the alumina content independently determined by chemical analysis also shown in Table 3.

TABLE 3. Summary of Measurement Results

<u>ROOM 4/POT 2</u>		<u>ROOM 4/POT 3</u>	
Bath Ratio	1.126	Bath Ratio	1.238
CaF ₂	4.8%	CaF ₂	5.08%
Alumina Content by:		Alumina Content by:	
Chemical Analysis	3.34%	Chemical Analysis	3.60%
Dip Cup Instrument	3.29%	Dip Cup Instrument	3.67%
<u>Set of Measured Transition Temperatures</u>		<u>Set of Measured Transition Temperatures</u>	
	937.8°C		956.5°C
	937.7		962.5
	943.0		958.9
	939.8		*
	945.9		958.4 **
	941.2		971.0
	946.7		971.0
	946.8		962.0
Mean Value	$T_m = 942.3^\circ\text{C}$		973.0
Standard Deviation	$s = 3.9^\circ\text{C}$		965.0
Standard Error	$v = 1.4^\circ\text{C}$	Mean Value	$T_m = 965.5^\circ\text{C}$
		Standard Deviation	$s = 6.1^\circ\text{C}$
		Standard Error	$v = 2.0^\circ\text{C}$

* Lost Dip Cup

** Data taken after new Dip Cup installed.

DISCUSSION OF ACCURACY

In the laboratory measurements taken at high concentrations of alumina with no CaF_2 , the standard deviation in the determination of alumina content was 0.17% or less. The measurements from this second field test at a production plant had much larger spread. A standard deviation of 3.9°C (Pot 2) for the transition temperature is equivalent to a standard deviation of 0.73% in the determination of alumina content. Any individual measurement of alumina content might vary from 2.56% to 4.02% where the Mean Value is 3.29%. Similarly, on Pot 3, with a standard deviation of 6.1°C in transition temperature, the corresponding standard deviation in the determination of alumina content would be 1.14% so that values of alumina content would vary from 2.54% to 4.82% on a mean value of 3.68%.

In order to obtain greater accuracy, it will be necessary to take a set of N measurements with N being about 9. In this way, a mean value is established which, for the transition temperature in the tests reported here, had a standard error of 1.4°C for Pot 2 and 2°C for Pot 3. This is equivalent to a standard error of 0.26% in alumina content for Pot 2 and 0.38% for Pot 3.

Further use of the instrument could point the way to improvements which would result in measurements of greater accuracy. It would seem that the repeatability observed in tests in the laboratory could be achieved in a production plant.

REVIEW OF PREVIOUS MEASUREMENTS

A set of measurements were taken at the Kaiser Mead plant on September 22, 1987. The results were reported to Rick James in a letter dated October 14, 1987, and in a memo dated October 7, 1987, to M. J. McMonigle of the U. S. Department of Energy. At the time there was no provision in the computational program to account for the CaF_2 content. Corrections to the reported results can now be made. The corrected values of alumina content are given in Table 4. Both Pots were in Room 48.

Table 4. Summary September 22, 1987, Measurements

<u>Pot</u>	<u>Bath Ratio</u>	<u>CaF_2</u>	<u>Transition Temperature</u>	<u>Calculated Alumina Content</u>
1	1.13	5.3%	935.4°C	4.94%
2	1.18	5.8%	956.3°C	3.60%

REFERENCES

Lee, S. S., K. S. Lei, P. Xu, and J. J. Brown. 1984. "Determination of Melting Temperatures and Al_2O_3 Solubilities for Hall Cell Electrolyte Compositions." In Light Metals 1984, Proceedings of the Technical Sessions Sponsored by the TMS Light Metals Committee at the 113th Annual Meeting, Ed. J. P. McGeer, pg. 841. The Metallurgical Society of AIME, Warrendale, Pennsylvania.

APPENDIX

ESTIMATES OF ACCURACY AND ERROR

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When a quantity Q is measured repeatedly, the values measured are generally found to differ somewhat from measurement. Let Q_i be the values determined in measurement number i . The Mean Value of a set of N measurements is the average value and is calculated using the equation

$$Q_m = \left(\sum_{i=1}^N Q_i \right) / N. \quad (A.1)$$

The limit of Q_m as N tends toward infinity is known as the Parametric Mean, M , of the quantity. Q_m may therefore be considered as an estimate of M based upon N measurements.

Standard Deviation is a measure of the accuracy of a single measurement in the determination of the Parametric Mean, M . However, since the true value of M is never known (we have only the estimates Q_m), Standard Deviation, s , is calculated using the equation

$$s = \text{SQR} \left(\sum_{i=1}^N (Q_m - Q_i)^2 / (N - 1) \right). \quad (A.2)$$

An estimate of the deviation of the value Q_m from the Parametric Mean, M , is known as the Standard Error and is given by

$$v = s / (N^{0.5}) = s / (\text{SQR}(N)). \quad (A.3)$$

In the case of the recent measurements at Kaiser Mead, the following results are obtained:

- Room 4 Pot 2

A set of 8 measurements of the transition temperature (assumed to be related to the liquidus Temperature) gave a mean value, T_m , of 942.3°C.

The standard deviation, calculated as indicated above, gave a value of $s = 3.9^{\circ}\text{C}$. The standard error would therefore be

$$v = 3.9/\text{SQR}(8) = 1.4^{\circ}\text{C}. \quad (\text{A.4})$$

- Room 4 Pot 3

A set of 9 measurements of the transition temperature gave a mean value, T_m , of 964.3°C with $s = 6.1^{\circ}\text{C}$ and $v = 2^{\circ}\text{C}$.

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