SLUDGE IN OPERATING ALUMINIUM SMELTING CELLS

Pierre-Yves Geay[1], Barry J. Welch[2] and Pierre Homsi[3]

(1) Aluminium Péchiney - LRF, B.P. 114, 73 303 Saint-Jean-de-Maurienne Cedex, France
pgeay@amt.pechiney.fr

(2) The University of Auckland, School of Engineering, Chemical & Materials Dpt, Private Bag 92019, Auckland, New Zealand
b.welch@auckland.ac.nz

(3) Aluminium Péchiney - Aluval, B.P. 7, 38341 Voreppe Cedex, France
phomsi@amt.pechiney.fr

Abstract

There has been growing concern on cathode wear in modern aluminium smelting cells, with doubts existing on the mechanistic causes. The dissolution of carbide has been shown to be an important factor, but there have been suggestions that abrasive wear is also a major contributor. The main abrasive in contact with the cathode blocks is the sludge but, to cause wear, it would have to have considerable mobility. Sludge also introduces a resistance to the current flow path since it has been shown that on some occasions it covers significant fractions of cathode surfaces.

In this investigation, the first stage was to take representative sludge samples and accurately characterize them by XRF, XRD, SEM-EDX and other chemical analytical methods. New phases have been identified and the sludge eutectic temperature has been more precisely defined. The second stage of the project was carried out to ascertain the location of sludge and its general mobility. The sludge level in pots was found to be very erratic but statistically, its average profile showed a correlation with the cathode wear pattern. Separate laboratory experiments demonstrate that the electrical conductivity of sludge is typically half that of normal electrolyte.

Introduction

Complete alumina dissolution on feeding is rarely achieved since some of the alumina particles sink to form sludge [1-3].

Other events like anode changing, metal tapping and anode effect also generate sludge: During the removal of the spent anode, lumps of crust fall in and if they are not removed properly, some remain at the bottom of the pot as sludge. After setting the new anode, typically 400 to 600 Kg of covering material are added and around 30% of this amount fall into the bath [4]. During metal tapping, the anode beam goes down a few centimeters in order to maintain the ACD. This important movement breaks the side channel crust, which falls in. And during the termination procedure of an anode effect, sludge is formed by both the overfeeding and through the crust collapsing in some areas of the pot.

Despite the great occurrence of sludge in pots, the literature on this topic is scarce. Accordingly, characterization of that material was carried out in this study.

Sludge composition

Sludge sampling

A tool was especially designed (Fig.1). After scraping the bottom of the pot, the tool was lifted vertically and the fluid metal drained while bath contamination was limited only to the outside parts of the sample. Cores of the samples were taken for analysis.
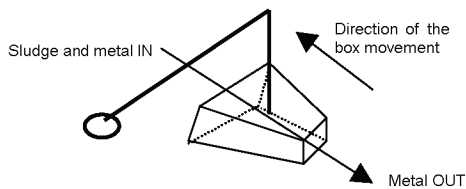

Figure 1: Scraping box for sludge sampling

Some sludge samples contained a black carbonaceous material that is probably cathode carbon (Fig.2-a). Frequently this black material was surrounded by a yellow layer (Fig.2-b).
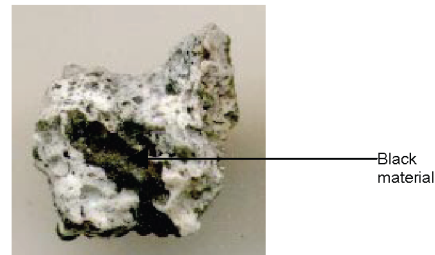

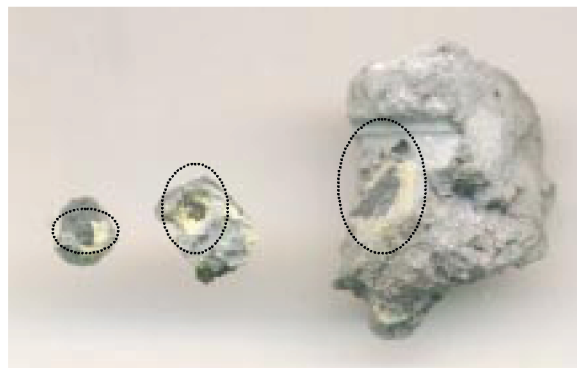Figure 2-a: Sludge picture, black material in sludge

Figure 2-b: Sludge picture, black material surrounded by a yellow layer

Sludge main phases

CaF_2 was determined by fluorescence, AlF_3 by a chemical method and Al_2O_3 by a classical chemical method using mass balance. Data obtained are summarized in Table I where they are also compared with previous results on sludge analysis [5].

Table I Phase percentages in sludge

SAMPLE	ELECTROLYTE			SLUDGE		
	Al_2O_3 (wt%)	xs AlF_3 (wt%)	CaF_2 (wt%)	Al_2O_3 (wt%)	xs AlF_3 (wt%)	CaF_2 (wt%)
Comalco (90)	/	8,2	/	42	2,5	/
Comalco	/	8,2	/	43	2,4	/
Comalco	/	8,6	/	41	2,3	/
Comalco	/	9,8	/	51	2,6	/
Comalco	/	12,8	/	39	5,2	/
Comalco	/	12,8	/	39	5,2	/
Tomago (99)	/	/	/	46	1,3	2,5
Tomago	/	/	/	43	0,3	3,2
St Jean (99)	3,6	13,3	4,7	39	1,2	2,8
St Jean	6,3	7,6	5,0	41	2,8	2,9
St Jean	6,3	7,6	5,0	49	2,0	2,4
St Jean	2,9	7,3	5,0	36	3,1	2,9
St Jean	2,9	7,3	5,0	41	2,5	2,7
St Jean	2,0	12,0	5,2	48	0,2	2,2
St Jean	2,6	12,7	4,9	34	2,5	3,4

Sludge typically contains about 40% alumina, 2% ALF_3 and 3% CaF_2. In contrast with a previous study [5], there was no correlation between the excess of AlF_3 in the electrolyte and the excess of AlF_3 in sludge. However, in general, the more alumina, the less additive. In particular CaF_2 correlated with the relationship,

$$\%CaF_2 = -6.3.10^{-2} \%alumina + 5.4 \qquad (1)$$

As sludge hardens at the bottom of the pot, it displaces the cryolite and additives, and the alumina grains cross-link in an alpha network. The different stages of sludge hardening explain the scatter in composition but it does not explain the full extent of the strong lowering in AlF_3.

Aluminium carbide in sludge

The yellow material in sludge (Fig.3) was identified by XRD as aluminium carbide (Fig.4). The main carbide peaks are distinct from the ones of the other components commonly present in the electrolyte, at 2ϑ-values of 32, 36, 40 and 55 with the easiest one to identify being at $2\vartheta = 55$.
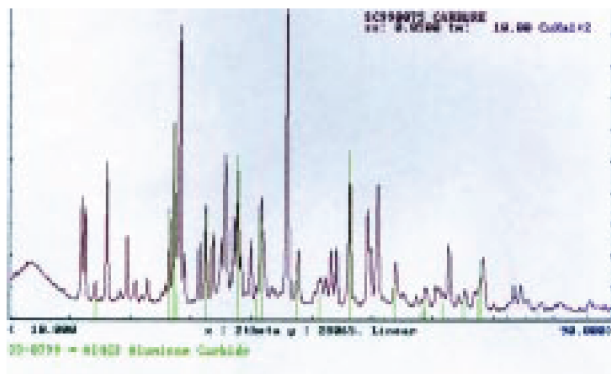

Figure 3: Yellow material in sludge

Figure 4: XRD spectrum of the yellow material found in sludge

In a sludge sample analyzed by XRD, aluminium carbide could be clearly identified which meant that this sample still contained at least 1 or 2% of aluminium carbide when the analysis took place. Aluminium carbide reacts indeed with air according to the following equations:

$$Al_4C_3 + 6O_2 => 2Al_2O_3 + 3CO_2$$
$$Al_4C_3 + 6H_2O => 2Al_2O_3 + 3CH_4$$
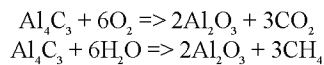
Therefore the samples have been stored under inert atmosphere to limit the degrading reactions.

Other materials in sludge

SEM-EDX allowed identification of carbon and aluminium metal in the sludge with aluminium droplets visible to the naked eye (Fig.5).
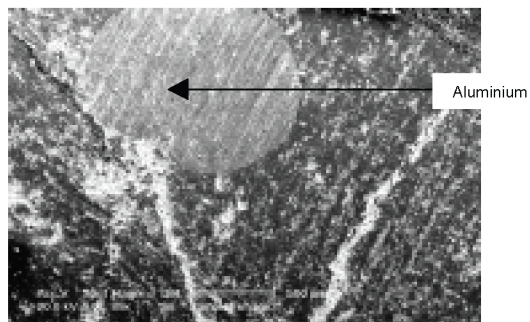

Figure 5: SEM picture of an aluminium droplet in sludge

Other metallic impurities such as iron, nickel, chrome and vanadium were also identified. They concentrated in the metal zones of the sludge. When fresh sludge is formed, it is enriched in the impurities associated with the raw materials added. Accordingly, since these impurities are readily reduced by the reaction,

$$Al + 3/x\ M^{x+} => Al^{3+} + M(Al)$$
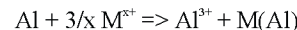
This would lead to the enrichment of impurities in some aluminium metal particulates as observed.

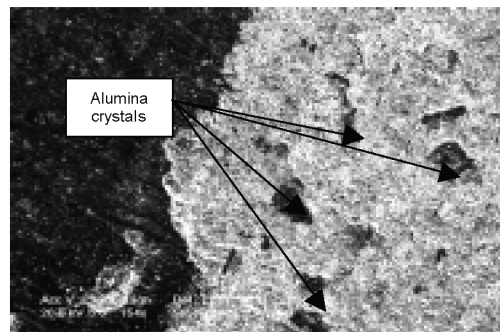Alpha alumina particles were also visible (Fig.6).

Figure 6: Alumina crystals in a sludge cryolitic phase

KF was also found in sludge and thanks to fluorescence, traces of silicon and phosphorous were also detected respectively, 120ppm and 40ppm in average.

Sludge eutectic temperature

Sludge is a two-phase material, a solid phase of alumina and a cryolitic liquid phase saturated with alumina. Total solidification occurs when the temperature decreases below the sludge eutectic temperature, T_e (Fig.7). For the analyzed sludges studied, the eutectic composition of the cryolitic liquid phase and thence its alumina saturated eutectic temperature were determined.

The proportions between AlF_3, CaF_2 and cryolite in the sludge liquid phase (e) are the same as the ones in the overall analyzed sludge samples (s):
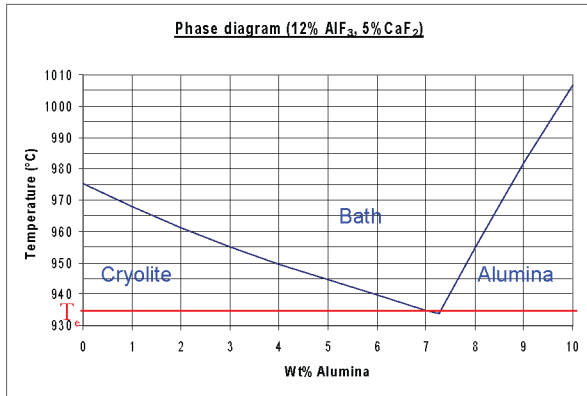
Figure 7: Alumina/Cryolitic melt phase diagram

$$[AlF_3]_e = k\,[AlF_3]_s \qquad\qquad (2)$$
$$[CaF_2]_e = k\,[CaF_2]_s \qquad\qquad (3)$$
$$[Cryolite]_e = k\,[Cryolite]_s \qquad (4)$$

and in each case,

$$[AlF_3]_e + [CaF_2]_e + [Cryolite]_e + [Al_2O_3]_e = 100 \qquad (5)$$
$$[AlF_3]_s + [CaF_2]_s + [Cryolite]_s + [Al_2O_3]_s = 100 \qquad (6)$$

$$T_l = f_l([AlF_3]_l, [CaF_2]_l, [Al_2O_3]_l) \qquad (8)$$
$$T_{sat} = f_{sat}([AlF_3]_{sat}, [CaF_2]_{sat}, [Al_2O_3]_{sat}) \qquad (9)$$

T_l, liquidus temperature.
T_{sat}, saturation temperature.
$[X]_l$, weight percentage of X at the liquidus composition.
$[X]_{sat}$, weight percentage of X at saturation.

The eutectic point corresponds to the intersection of the liquidus curve with the alumina saturation one and then $T_l = T_{sat}$. Therefore, from equations (8) and (9),

$$f_e([AlF_3]_e, [CaF_2]_e, [Al_2O_3]_e) = 0$$

With equations (2), (3) and (7),

$$f_e(k\,[AlF_3]_s, k\,[CaF_2]_s, 100 - k\,(100 - [Al_2O_3]_s)) = 0$$

$[AlF_3]_s$, $[CaF_2]_s$ and $[Al_2O_3]_s$ are known for each sludge sample, so finally we get the following equation to solve for each sludge composition,

$$g_e(k) = 0$$

Results are shown in Table II.

Table II Sludge eutectic phase characteristics

SAMPLE	SLUDGE			EUTECTIC LIQUID					k
	Al_2O_3 (wt%)	xs AlF_3 (wt%)	CaF_2* (wt%)	Al_2O_3 (wt%)	xs AlF_3 (wt%)	CaF_2 (wt%)	T_e (°C) calc.	T_e (°C) DTA	
Comalco (90)	42	2,5	2,7	8,6	3,9	4,3	954	955	1,575
Comalco	43	2,4	2,6	8,7	3,8	4,2	954	956	1,602
Comalco	41	2,3	2,8	8,7	3,6	4,3	954	957	1,548
Comalco	51	2,6	2,1	8,6	4,8	4,0	953	955	1,865
Comalco	39	5,2	2,9	8,1	7,8	4,4	945	948	1,507
Comalco	39	5,2	2,9	8,1	7,8	4,4	945	947	1,507
Tomago (99)	46	1,3	2,5	8,8	2,2	4,2	955	/	1,689
Tomago	43	0,3	3,2	8,7	0,5	5,1	954	/	1,602
St Jean (99)	39	1,2	2,8	8,8	1,8	4,2	956	/	1,494
St Jean	41	2,8	2,9	8,5	4,3	4,5	953	/	1,550
St Jean	49	2,0	2,4	8,7	3,6	4,3	954	/	1,791
St Jean	36	3,1	2,9	8,6	4,4	4,1	953	/	1,428
St Jean	41	2,5	2,7	8,7	3,9	4,2	954	/	1,548
St Jean	48	0,2	2,2	9,0	0,4	3,9	957	/	1,750
St Jean	34	2,5	3,4	8,6	3,5	4,7	954	/	1,385
AVERAGE	42	1,8	2,8	8,7	2,7	4,4	954	953	

* CaF_2 in sludge for Comalco samples was calculated with equation (1)

with,
$[X]_e$, weight percentage of X in the sludge liquid phase.
$[X]_s$, weight percentage of X in the sludge overall sample.
k, proportionality coefficient.

Using equations (2) to (6),

$$[Al_2O_3]_e = 100 - k\,(100 - [Al_2O_3]_s) \qquad (7)$$

Liquidus temperature and alumina solubility have been reviewed and two equations could be set [6]:

The calculated eutectic temperature using this method for Comalco samples is only 1 to 3°C under the one measured by Differential Thermal Analysis [5]. Thus the proposed method is reasonably accurate for sludge eutectic temperature and composition calculations. It can be concluded that in average the sludge eutectic phase is saturated with 9% alumina and contains approximately 3% AlF_3 and 4.5% CaF_2. For the different smelters, the sludge eutectic phase had almost the same amount of CaF_2 as the bath but was far less acid. Its solidification temperature is 954°C which is significantly above that for normal bath.

Sludge electrical conductivity

Sludge is known to increase the cathode voltage drop but currently no data exists that enables correlation between this, the amount of sludge and the cell disturbances. Fundamental to developing an understanding is the knowledge of the electrical conductivity of the sludge.

A laboratory aluminium smelting cell was designed to measure sludge electrical conductivity (Fig.8 and 9). The bath had a typical industrial composition except that it was saturated with 10% alumina. The targeted temperature was 960°C.
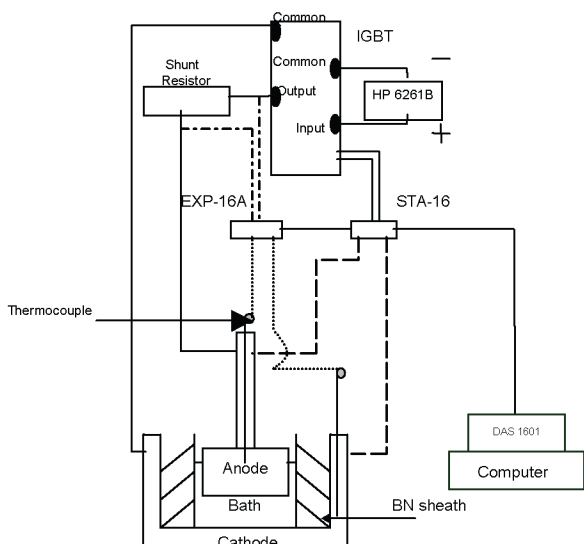

Figure 8: Arrangement for sludge electrical conductivity measurement
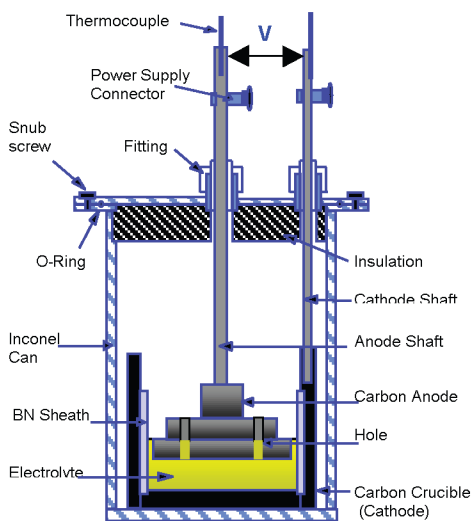

Figure 9: The laboratory electrolysis cell

Sludge was formed by adding an excess of alumina to the cell and this was confirmed at the end of an experiment by sectioning the crucible where two different layers could be observed. The boron nitride sheath in the crucible ensured unidirectional current flow. The data acquisition took place at a 40Hz frequency.

The cell voltage V is the sum of [7]:
- E : Nernst potential
- η : Anodic and cathodic overvoltage
- $V_{bubbles}$: CO_2 bubble voltage
- V_{bath} : Bath voltage
- V_{sludge} : Sludge voltage
- V_{ext} : External voltage

Using the high-speed cell switch IGBT (Insulated Gate Bipolar Transistor), when the current is switched on and off, the ohmic contributions can be separated from the Nernst and polarization potentials (Fig.10).
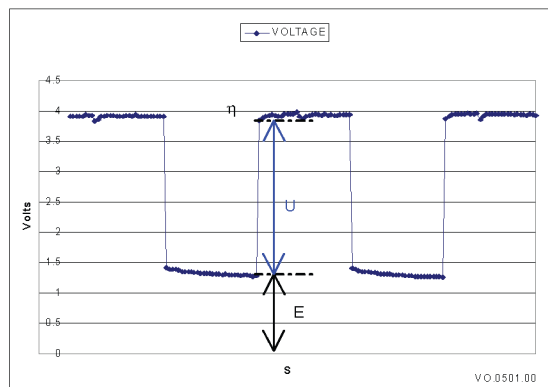

Figure 10: Voltage breakdown with the IGBT

The impact of the bubble voltage was minimized by having very short electrolysis times. Then,

$$U = V_{bath} + V_{sludge} + V_{ext}$$

As the external voltage is constant before and after sludge formation,

$$\Delta U = \Delta V_{bath} + \Delta V_{sludge}$$

$V = j \, h \, / \, k$,   j, current density
   h, length of the electrical medium
   k, electrical conductivity of the medium

$$k_{sludge} = \cfrac{1}{1 + \cfrac{\Delta U \, k_{bath}}{j \, \Delta h}} \, k_{bath}$$

j was fixed by the intensity going into the cell.
ΔU was measured by the experimental device.
k_{bath} could be measured by moving the anode up or down from a known distance. The experimental measurements were in very good agreement with the literature [8]. Bath electrical conductivity did not vary before and after sludge formation.
Δh, the height of sludge which had formed in the crucible was difficult to assess experimentally as the sludge was soft. However it could be calculated.

Experiments gave :   **k_{sludge} = 1.0 S/cm ± 0.2**

Soft sludge electrical conductivity is typically half that of a classic electrolyte.

Extent of sludging in an operating cell

Small ditches were carefully dug between the anodes in order to fit a harp jig (Fig.11). The limits between the bath, the metal and the sludge could be clearly identified on the rods with an accuracy of 0.5cm. The small amount of crust falling into the bath did not interfere significantly.
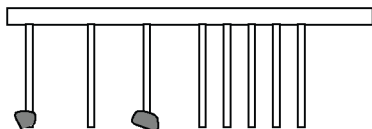
Figure 11: The harp jig

This device gave a good measure of the sludge level in different locations but less than the first third of the anode length could be reached in practice. Therefore only two pots were probed this way, one AP18 (Table III) and one AP28 (Table IV). The number after the rod indicates its position from the deck plate in centimeters.

Table III Sludge level measurements with the harp jig (AP18)

AP 18	Sludge level (cm)						
Ditch	Rod 40	Rod 45	Rod 50	Rod 55	Rod 65	Rod 75	Rod 85
1 - 2	0	0	0	4	0	0	8
4 - 5	0	0	0	0	0	10	12
9 - 10	0	4	0	3	0	10	14
12 - 13	0	0	0	2	0	0	0
15 - 16	0	0	0	4	7	0	0

Table IV Sludge level measurements with the harp jig (AP28)

AP 28	Sludge level (cm)							
Ditch	Rod 35	Rod 40	Rod 45	Rod 50	Rod 55	Rod 65	Rod 75	Rod 85
4 - 5	0	0	0	0	0	0	0	0
6 - 7	0	0	0	0	0	0	9	0
8 - 9	0	0	0	0	0	2	0	0
12 -13	0	0	0	4	0	3	0	0
14 - 15	1	0	0	0	0	7	0	3
16 - 17	4	5	0	0	0	0	0	9
18 - 19	0	0	0	0	2	0	3	0

It is interesting to notice that sludge level is very erratic for very short distances, indicating that sludge does not move much in these magnetic compensated pots.

Another series of sludge level measurements was carried out to assess the general sludge profile in the pots. A set of pots was chosen and prior to anode change, several rods were positioned in holes around the spent anode. In recording these, the upstream and downstream sides were divided in 10 parts: D10 referred to the downstream side channel, D9 the extremity of the downstream anode,..., 0 the center channel,..., till U10 the upstream side channel. A total of 432 sludge height measurements were made. There was no evidence of a correlation between an anode number and the related average sludge accumulation in its area. The most interesting result was the average sludge profile in the pots (Fig. 12), which looks close to a typical cathode wear profile.

It is probable that sludge levels are higher in the vicinity of the center channel for three reasons:
- Alumina feeding takes place in the center channel and when the alumina does not dissolve properly, sludge forms there.
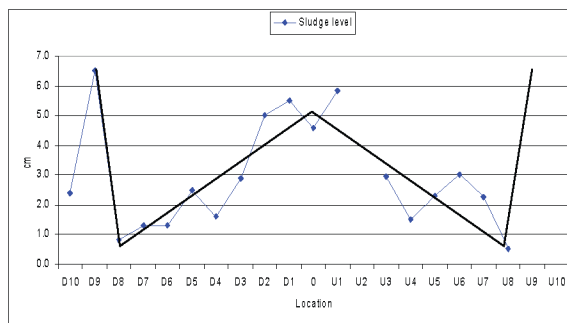
Figure 12: Sludge profile in pots∗
∗Locations with fewer than 4 measurements are not represented

- The crust is fragile in that area and can collapse, forming sludge.
- During covering practices, a lot of material is added in the center channel, making more sludge in that area.

Hard sludge, which cannot be probed, has probably the same profile as the one measured above as this material also called ridge sometimes, comes from sludge hardening. For some pots, the liquid level, metal + bath, was 10cm lower in the center channel than between the anodes. The swelling and wear of the cathode cannot explain entirely this gap. This difference was probably also due to a big accumulation of ridge in the center channel.

Sludge influence on cathode wear

Sludge, a diffusion barrier

The cathode wear rate decreases in a stirred melt oversaturated with alumina [9]. Sludge probably acts as a mass transfer barrier retarding wear. Moreover, in the case of sludge, it has been shown that it probably does not move much. Therefore there is no abrasive effect from sludge. As the cathode wear and sludge profiles are similar, it can be concluded that sludge protects the area on which it settles.

Influence of sludge on the current distribution

As sludge is a more resistive material, its uneven distribution has an influence on the current distribution. A simple electrical model was used for calculation (Fig.13).
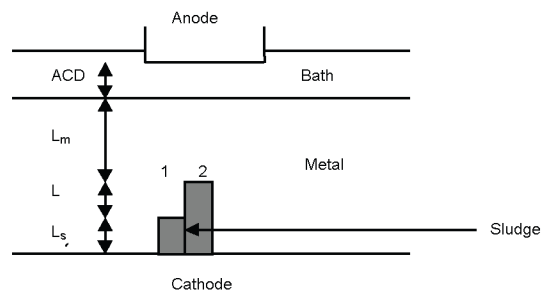
Figure 13: Electrical model for sludge electrical influence calculation

The relative resistance of the electrical pathways 1 and 2 is:

$$\frac{R_2}{R_1} = \frac{k_{Sludge}\,ACD + k_{Bath}\,L_s + k_{Bath}\,L}{k_{Sludge}\,ACD + k_{Bath}\,L_s} \qquad (10)$$

Results using equation (10) are shown in Table V. The following values were chosen for calculation: k_{Sludge} = 1.0 S/cm, k_{Bath} = 2.1 S/cm, ACD = 5 cm and j = 0.8 A/cm^2.

Table V Influence of sludge on the current density

| L_s (cm)	L (cm)	j_1 (A/cm^2)	j_2 (A/cm^2)
0	1	0,9	0,7
0	3	1,1	0,5
0	10	1,3	0,3
2	1	0,9	0,7
2	8	1,2	0,4
4	6	1,1	0,5
6	4	1,0	0,6

Sludge uneven distribution creates preferential current pathways where the current density is much higher than the average current density. As the wear rate increases with current density [10], these areas are more sensitive to corrosion. This effect is probably even stronger with ridge.

Sludge and aluminium carbide

In the above explanation, it should be noted that conduction through the sludge is via ionic transport. Since there is a potential gradient, the metal surface is more anodic than the carbon cathode (even though both are cathodic). This current flow can explain the presence of carbide, carbon particulate and the composition of the sludge liquid phase. The anodic dissolution reaction that is probably more favored at the metal/sludge interface is:

$$Na(Al) + F^- => NaF + e^-$$
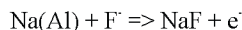
At the cathode, carbide is electrochemically favored and therefore we would have:

$$3C + 4Al^{3+} + 12e^- => Al_4C_3$$
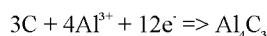
The aluminium carbide would be soluble in the electrolyte whilst acidic, but precipitate out when the electrolyte becomes saturated, or the composition changes to being more alkali. Thus, with time, the sludge would assume a new steady state, more alkali composition, as is found.

The formation of the carbide can also occur in the electrolyte-saturated pores of the cathode surface. Such growth could lead to a weakening of carbon particulate. Such carbon particulate would then reside in the sludge, as was observed, and would normally be surrounded by aluminium carbide. It is also consistent with other studies described elsewhere in this Proceedings [11].

Conclusion

Sludge is a complex mixture with 40% alumina, 2% aluminium fluoride, 3% calcium fluoride and about 2% aluminium carbide. It also contains carbon, aluminium metal and impurities such as Si, Cr, V, Ni and P. 0.1% of iron was also detected.

Sludge liquid eutectic composition is 9% alumina, 3% aluminium fluoride and 4.5% calcium fluoride. Its solidification temperature is 954°C. Therefore pots should not be run under 955°C to avoid any operating problems due to sludge.

Once sludge settles on the cathode, it acts like a barrier which reduces corrosion. However its uneven distribution is harmful for the unprotected parts of the cathode.

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