

INVESTIGATION OF THE CORROSION PROBLEM IN THE PIPELINE OF ENRICHED ALUMINA RECYCLE TO ALUMINIUM CELL

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In this work, the failure of pipeline used for recycling the enriched alumina to self-baked (Soderberg) cells is investigated; the study includes also the deterioration of pipeline that recycling the enriched alumina to pre-baked cells and that recycling fresh alumina. Systematic measurements for the loss in the pipeline –wall thickness with the time are carried out. The gaseous emissions from the cells and the characteristics of enriched alumina are analyzed. Based on the analyses and visual inspections, a corrosive- wear sequence was identified, for the failure of pipeline of Soderberg system. The scales formed on the pipe inner wall are easily destroyed by the alumina impact due to the weak adherence of such scales. This resulted in the exposure of the fresh steel surface to the highly corrosive environment that prevails inside the pipeline, which accelerates the corrosion of the metal. For the pipeline recycling enriched alumina of pre-baked system, hard and dense layers were formed, which were strictly adherent to substrate. The loss in the pipeline wall thickness of the fresh and pre-baked alumina pipelines is negligible compared to Soderberg enriched line (0.5 versus 5.0 mm/year); however, the operating conditions of the particles impact (velocity, particle size, flux) were close to each other in value. Therefore, the failure mode of pipeline in the Soderberg system is an erosion-corrosion process.

KEYWORDS: *Erosion-corrosion, Pipeline failure, aluminium smelting cell, Gaseous emissions, Carbon steel.*

1. INTRODUCTION

In the aluminium smelting technology there are two cell types, the Pre-baked and the self-baked (Soderberg cell) .The principal difference between them is the type of anode used. Soderberg technology uses a continuous anode which is delivered to the cell in the form of a paste, which bakes in the pot itself. Prebaked technology, on the

other hand, uses multiple anode blocks in each cell. These anode blocks are pre-baked in a separate facility and then delivered to the cell.

Emissions of fluorides from the smelting process, in gaseous and particulate form, were earlier considered to be the most important pollutants from smelting. Modern control systems to remove and recycle fluorides through gas collection and wet/dry scrubbing systems have largely eliminated the problem. In Naga Hammadi Misr aluminium company the cell gases go through a dry cleaning stations to capture mainly HF gases and the particulate fluoride salts. In the cleaning stations, there are pipelines and storage vessels for handling fresh alumina and others for handling enriched reacted alumina before being recycled to the cells. Pneumatic transportation system is used for conveying the fresh and enriched alumina. The main reaction occurring between fresh alumina and gases is the chemisorption of HF on the alumina (enriched alumina) to form AlF_3 [1]. It was observed that after about 6 months operation a severe damage arised in the enriched alumina lines for Soderberg cell gases. However, there was a mild damage in fresh alumina lines and the lines of pre-baked system whether transport fresh or enriched alumina. This may be attributed to the high concentration of corrosive agents, detected in the Soderberg pipelines, which promote the deterioration of the steel pipe, mainly due to erosion – corrosion. Figure 1 shows the erosion –corrosion problem in the transportation line of Soderberg cells. In addition to that ,the corrosion product can be introduced to the cell bath, which may contaminate the purity of the aluminium products . This has a substantial effect on the aluminium industry profitability, since aluminium quality is a key aspect of the export market.

Despite the extensive work done in the past, there has been no clear understanding of erosion-corrosion interaction in the field condition. Hence, the aim of this work is to study erosion –corrosion due to abrasion and corrosive agents flowing in the pipelines. In order to achieve the research objectives, the thickness loss rate is measured at different locations of cross –sectional area and different conditions, the circulating constituents of pipes are analyzed, the gases of cells are analyzed and the effect of erosion-corrosion product on the aluminium purity is checked.

2. EROSION-CORROSION

Corrosion is a material degradation process which occurs due to chemical or electro-chemical action, and erosion is a mechanical wear process (e.g. impact of solid particles) [2]. When these two processes act together the conjoint action of erosion and corrosion in aqueous is known as erosion-corrosion. This phenomenon is known to cause premature failure in the equipment used in engineering applications. In other words, the combined effect of erosion and corrosion can be significantly higher than the sum of the effects of the processes acting separately [2, 3, and 4]. This net effect is called synergism. As proposed by many researchers, this net effect is due to the enhancement of corrosion by erosion and/or enhancement of erosion by corrosion [5]. The wastage of material in erosion-corrosion process according to the mechanism of material loss is considered a contribution of electrochemical corrosion and mechanical erosion:



(a)



(b)

Fig. 1: Photographs of the erosion –corrosion in the pipeline of Soderberg cells; a- inlet of the pipeline, b- failure of the inner pipe

$$W_t = W_c + W_e \quad (1)$$

Where:

$$W_c = W_c^0 + W_c^e \quad \text{And} \quad (2)$$

$$W_e = W_e^0 + W_e^c \quad (3)$$

Where, W_t is the total mass loss of the material, W_c is the corrosion component with the presence of erosion, W_e is the erosion component with the presence of corrosion, W_c^0 is the corrosion component free of erosion, W_e^0 is the erosion component free of corrosion, W_c^e is the corrosion component promoted by erosion and W_e^c is the erosion component enhanced by corrosion.

The total material loss caused by erosion-enhanced corrosion and corrosion-enhanced erosion is often regarded as the wastage produced by the synergistic effect, W_s

$$W_s = W_c^e + W_e^c \quad (4)$$

In most cases, W_s is greater than zero because the mechanical erosion and electrochemical corrosion interact and accelerate each other concurrently. Such a synergistic effect leads to a dramatic increase in damage rate.

Although the problem caused by the interaction of erosion and corrosion is very serious, the mechanism of synergy is still not thoroughly understood because of its complexity. Postlethwaite [6] proposed that corrosion increases erosion rate by roughening the metal surface, because erosion rate is very sensitive to the impingement angle of solid particles. Li et al. [7] suggested a new mechanism that the localized attack at disruptions in the surface oxide (caused by the particle impacts) enhances the rate of the crack growth, causes the flakes to become detached and then leads to higher erosion rate. Matsumura et al. [8] pointed out that erosion can be enhanced by corrosion through the elimination of the work-hardened layer. Recently Malka et al. [9] have looked at whether erosion enhances corrosion and/or corrosion enhances erosion in pipe loop experiments on AISI 1018 carbon steel in 2 wt.% silica sand ($275\mu\text{m}$). They found that erosion enhances corrosion and corrosion enhances erosion but the dominant synergistic effect was that of corrosion on erosion.

3. SYSTEM UNDER INVESTIGATION

Associated with the EGYPTALUM pot lines there are gas treatment centers (GTC'S) that is positioned between the pot rooms to receive emissions from the pots. The GTC'S have the primary role of recycling the fluoride and dust captured from the pots. The emissions are treated in the GTC to extract the fluoride, using alumina as a scrubbing agent. The fluorinated alumina is then directed into the pots. Figure 2 shows the schematic of the pipeline network with the necessary storage bins and silos for one of GTC'S. The pipelines 5, 7 and 6, 8 are used for carrying enriched alumina and fresh alumina respectively. The pipeline material is carbon steel. The chemical analysis of the carbon steel is carried out by an optical emission spectrometry "ARL 3560" and is given in Table 1. The pipeline has an inside diameter of 127mm and thickness of 6mm. The pipeline length is 300m, in which 260m is horizontal and 40m is vertical. The pipeline consists of connecting tubes of 6m long. The tube is seamless with flanged connections. In this study, the failure analysis is concerned with the horizontal pipeline. The air required for conveying the particulate material within the pipeline is jetting from small tube 20mm diameter incorporated within the pipeline. The air velocity is measured by a pitot-tube meter which is already erected in the pipeline construction. The loss in thickness of the inner side of the pipe wall is investigated for pipelines 6,11,5 and 7. Pipeline 6 transports fresh alumina. Pipelines 11, 5 and 7 deals with enriched alumina. Pipeline 11 belongs to the prebaked system while pipelines 5 and 7 belong to the Soderberg system. The pipe wall thickness is measured by a

portable ultrasonic thickness meter (DM2) having an accuracy of 0.1mm. The loss in thickness is the difference between the thickness before and after a definite period at the same location.

Table 1: Chemical composition of the pipeline material

Element	C	Mn	P	Si	Cu	Ni	Cr	Mo
wt %	0.08	0.55	0.007	0.018	0.019	0.023	0.025	0.008

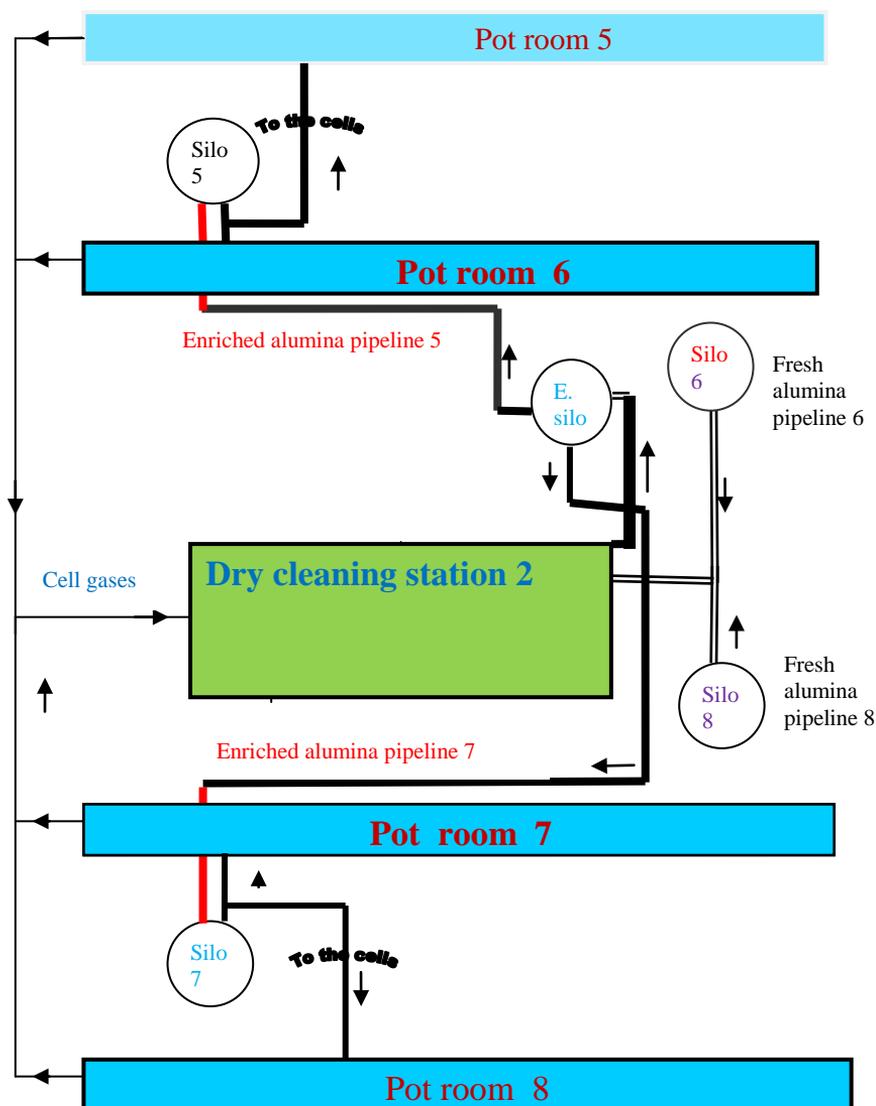


Fig.2: Schematic diagram for the Soderberg pipeline system

4. RESULTS

4.1 Measurements of the thickness loss rate

The loss in the thickness of the inner side wall of horizontal pipelines is measured at three points. Two points (1&2) at the ends of the horizontal diameter. The third one (3) at the bottom end of the vertical diameter. These measurements are repeated along the pipeline at a span of 60 cm. Tables 2 and 3 show typical measurements for the loss in thickness along the circumferential and longitudinal tube wall, respectively. The data reported in Table 2 belong to pipeline 5 and those at Table 3 belong to pipeline 7. From Table 2, it seems that the largest loss in the thickness is at the bottom (point 3). Therefore, the loss in the thickness at the bottom will be taken into consideration in analyzing the failure for different pipelines. Figure 3 and Table 3 show that the most deteriorated region is beside the flange.

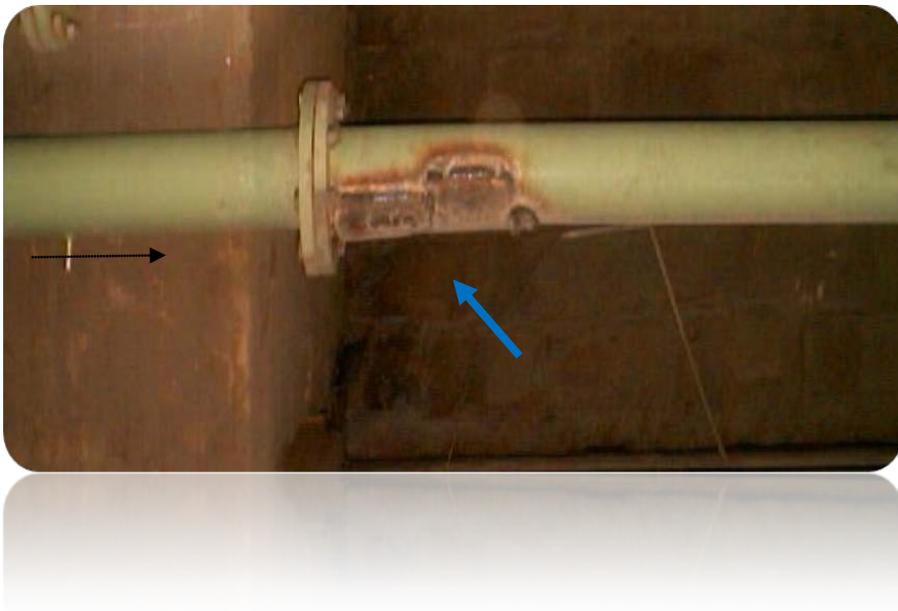


Fig. 3: Photograph of the more deteriorated locations

Table 2: Thickness loss distribution along circumferential tube wall

Circumferential point	1	2	3
Average loss ,mm/year*	0.62	0.68	1.79

(* averaged over 81 reading)

Table 3: Thickness loss distribution along the tube wall length

Length apart from flange, cm	60	120	180	240	300	360	420	480	540
Average loss, mm/year	2.07	1.85	1.91	1.87	1.84	1.99	1.92	1.85	1.91

The loss and loss rate in the thickness for different pipelines working at different field conditions are shown in Table 4. The data presented in this Table are the average of 30 ~ 80 measurements. It is clear from this Table that pipelines 5, 7 and 11 that transport enriched alumina have a higher loss rate than that transporting fresh alumina, i.e. pipeline 6. However, the loss rate of pipeline 11, which belong to pre-baked cells about 20% more than that of pipeline 6. This means that the loss rate in the thickness of pipeline 6 and 11 is within the acceptable range and the erosion-corrosion effect is mild. The high rate for pipelines 5 and 7 belongs to Soderberg cells. The loss is about 7-10 times that of pre-baked and fresh pipelines respectively. With regard to the effect of the velocity of air carrying the particulate material, the lower loss rate is the higher velocity, as shown in Table 4. It is presumed to occur the opposite, if the erosion is the dominant in the failure, since the erosion is an exponential function of the velocity. This interprets that the failure mechanism of the pipelines in the Soderberg system is different from that prevailed in the pipelines of the pre-baked system. The data of Table 4 indicate an increase in the loss rate by a decrease in air velocity, which may suggest different erosion mechanism at a low velocity.

4.2 The effect of pipe wall degradation on the purity of molten aluminium.

To illustrate the effect of pipe wall degradation on the purity of the aluminium product, the iron content of molten aluminium in two pot rooms is analyzed. The first pot room (NO.6) is fed by enriched alumina that is conveyed by highly degraded pipeline 5 of Soderberg system. However the second pot room (NO.4) is not fed by enriched alumina, so the pipe wall degradation conveyed to this pot room is very little or negligible. The iron content is measured every month and repeated along 9 months, as shown in Table 5. The data indicate that the iron content in pot room (No. 6) is larger than that in pot room (No. 4). This reflects the deleterious effect of pipe wall degradation on the quality of the aluminium product.

4.3 Analysis of the scale formed on the inner pipeline wall

To obtain general understanding of the severe damage encountered, preliminary analysis on samples collected from pipeline 11 (pre-baked system) and pipelines 5 and 7 (Soderberg system) are carried out. The qualitative analysis of the scales is carried out using a computer controlled diffractometer "D4 ENDEAVOR" and given in Table

6. The quantitative analysis of scale of pipeline 11 is achieved by sequential computer X-ray fluorescent "SRS 3400". And found to be: 8.1 Na, 32.8Al, 8.4 F, 0.06 Si. The analyses of samples of pipeline 11 show that the main components are alumina and salts of cell bath components and not corrosion products. However, the analyses of scales collected from pipelines 5 and 7 illustrate that they are corrosion products.

Table 4: The loss and loss rate in thickness of different pipelines

Pipe line	Average loss in thickness, m	Nominal operation time, months	Actual operation time, month	Thick. loss rate, mm/year	Velocity of air, m/s	Recycled particulate	Cell type
6	0.6	30	16.25	0.44	49	Fresh alumina	Both types
11	2.85	84	63	0.54	49	Enriched alumina	Pre-baked
5	2.99	20	10.83	3.31	37	Enriched alumina	Soderberg
7	2.8	12	6.5	5.16	31	Enriched alumina	Soderberg
5	0.7	3	1.62	5.18	31	Enriched alumina	Soderberg

Table 5: The iron content of molten aluminium, monthly measured, wt %

Period pot room	1	2	3	4	5	6	7	8	9	Av.
Pot room 6	.175	.170	.229	.178	.197	.239	.220	.208	.187	.200
Pot room 4	.141	.130	.115	.133	.139	.140	.141	.145	.146	.136

Table 6: Analysis of the scale collected from pipelines

Sample	Phases identified
Scales of pipeline 11	Alumina (Al_2O_3)- Cryolite (NaF-AlF_3) Chiolit ($\text{Na}_5\text{-AlF}_{14}$)
Scales of pipeline 5	Iron hydroxide { $\text{Fe}(\text{OH})_3$ } Iron oxide { $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ }

Analysis of cell gases

Aluminium cell exhaust gases contain particulates, such as dust and solidified cell content; tar; gases, such as CO₂,CO,SO₂,etc. ; and some vaporized fluoride compounds and H₂O. The analysis of cell gases in the Soderberg and pre-baked systems are shown in Table 7. The Soderberg technology has higher emissions compared with that for pre-baked technology.

Table 7: Analysis of the species present in the fumes from smelting cells.

System	Soderberg	Pre-baked
Hydrogen fluoride, HF	250mg / m ³	180mg / m ³
Sulphur compounds given as SO ₂	400mg / m ³	34.5mg / m ³
Tar content	100mg / m ³	-
Dust content	2000mg / m ³	65mg / m ³
Water vapour	10000mg / m ³	-

4.5 Alumina characterization

The fresh alumina (Al₂O₃) has white color. However as result of passing the emission gases in the bed of fresh alumina for cleaning, the alumina has discolored. The worst discolor was for the enriched alumina used in the Soderberg system. The color changed from white to cinnamon.

SEM photographs of the fresh alumina and the enriched alumina used in the pre-baked and Soderberg are shown in Fig.4. It is difficult to identify any change in the structure among the different alumina samples

The enriched and fresh alumina was analyzed to detect the components which may affect the pipe wall degradation. These analyses were carried out using X-RAY fluorescent (SRS 3400) and it is shown in Table 8. Loss on ignition (L.O.I) occurred between 300 and 1000 centigrade was the highest for enriched alumina used in Soderberg system. This higher moisture content manifests the increase in adsorption capacity in Soderberg [10].

5. DISCUSSION

From the results shown above, the loss in thickness of pipeline wall of Soderberg system was 7 and 10 times that of pre-baked system and pipeline handling fresh alumina, respectively. The difference in operating conditions such as; velocity, size, and flux of particles is not much and can not be considered behind these results.

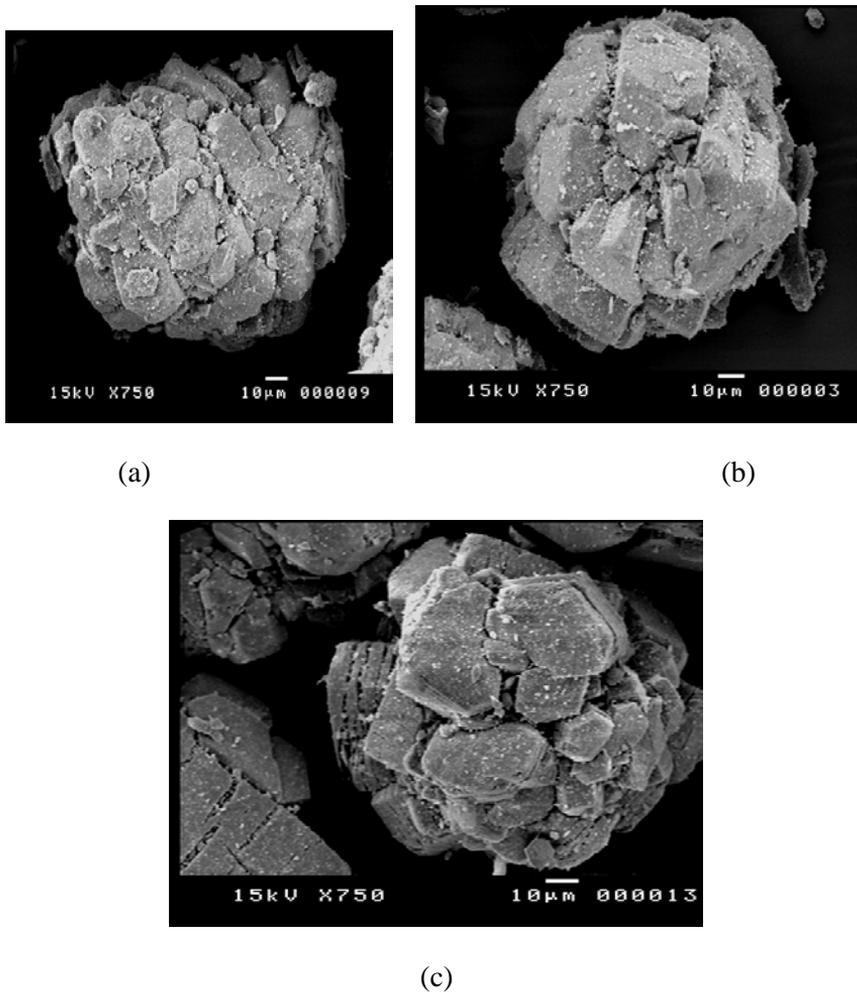


Fig.4: SEM photographs of the enriched alumina used in the Soderberg system (a), enriched alumina used in pre-baked system (b) and fresh alumina (c)

For pipelines of the pre-baked system, there is a resistance to the erosion-corrosion process because of the formation of protective cake layers. These layers are examined and found to be hard, dense and strictly adherent to the substrate. These layers are composed of salts of cell bath components; cryolite and chiolite as indicated in Table 7. These salts have been entrained with the cell gases as a vapor or particulate. It can be said that for the pipeline of pre-baked system, a negative synergy occurs, which is called an antagonistic effect [11]. The reduction in corrosion rates ($-W_e^c$) could result from the rapid coating growth on the pipeline wall.

The enhancement of erosion by corrosion occurred in pipelines of Soderberg system, might be attributed to the large amount of aggressive corrosive agents emitted from these cells (Table 8). These gaseous emissions leave the cell and pass through ducting to an alumina dry scrubbing system. The alumina used in the dry scrubbers (enriched alumina) is recycled to the cells, along with any impurities and adsorbed

gases collecting during scrubbing. The primary reason for dry scrubbing is to remove HF, impurities (Fe, Ni, V) and particulate fluorides from electrolyte bath (NaAlF₄, Na₃AlF₆, Na₅AlF₁₄) [12]. However, as these emissions are efficiently captured in the dry scrubber, some attention has been focused on the emissions of lesser gases [13]. Capture of these other emissions can have downstream consequences on the alumina (see Table 8) from the dry scrubbers recycled into the cells [10]. Inability to capture these emissions could become problematic.

Another reason for the encountered problem is the accumulation of enriched alumina on the pipelines during the stagnant period. This will accentuate the corrosion process especially at the bottom of the pipelines, as it is observed in Table.

Table (8): The analyses of enriched alumina and fresh alumina

Specification	Units	Results		
		Soderberg	Pre-baked	Fresh
F	%	1.07	1.15	-
S	%	0.17	0.21	-
C	%	0.2	0.1	-
SiO ₂	%	0.005	0.005	0.008
Fe ₂ O ₃	%	0.018	0.012	0.008
Na ₂ O	%	0.55	0.46	0.40
CaO	%	0.05	0.04	0.32
Moisture(at 300 C)	%	0.69	0.66	0.40
L.O.I (at 1000 C)	%	2.2	1.6	0.87
Bulk density	<i>g / cm³</i>	0.98	1	0.95
Angle of repose	degree	30	30	33
Sieve Analysis:				
+150 micron	%	1.61	5.64	5
-45 micron	%	4.23	4.21	6

6. CONCLUSIONS

1. The failure of pipeline recycling enriched alumina to Soderberg cells was due to erosion-corrosion. However, the dominant process was the effect of corrosion on erosion.

2. The adsorbed gases on enriched alumina in Soderberg systems contains several corrosive agents, which accelerated corrosion.
3. In pipeline recycling enriched alumina to the pre-baked cell, rapid coating growth was formed on the pipeline wall. This could result in the reduction in corrosion rate.
4. The system design and operation need to be improved so that the erosion-corrosion problem can be controlled, e.g., the stagnant period, the cleaning of pipeline from the enriched alumina, the versatile change of air velocity,...etc

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فحص مشكلة التآكل في خطوط أنابيب الالومينا المشبعة الراجعة إلى خلايا الالومنيوم

في هذا البحث تم دراسة تدهور خطوط أنابيب نقل الالومينا المشبعة الى الخلايا ذاتية التحميص وشملت الدراسة ايضا التآكل في خطوط انابيب نقل الالومينا المشبعة الى الخلايا سابقة التحميص وكذلك خطوط نقل الالومينا الخام. ولمعرفة أسباب التآكل تم قياس سمك الانابيب ومعدل الفقد في السمك مع الزمن ،وكذلك تم تحليل الغازات المنبعثة من الخلايا وكذلك الخواص الكيميائية و الفيزيائية للالومينا المشبعة والالومينا الخام. وبناءا على هذه التحليلات والقياسات والفحوصات وجد أن تدهور خطوط الأنابيب يرجع إلى وجود تآكل كهروكيميائي/ميكانيكي بالتأثير المتبادل ،حيث يتم تعرية سطح خطوط الأنابيب من القشرة المكونة بفعل اصطدام حبيبات الالومينا ،وذلك لضعف التصاقها بالسطح . وهذا الفقد يعمل على توليد سطح جديد من المعدن و الذي يتفاعل بدوره مع العوامل المنشطة للتآكل والموجودة بالانابيب،وباستمرار هذا الإجراء تتدهور هذه الأنابيب في وقت قصير . أما بالنسبة للأنابيب الخاصة بالخلايا سابقة التحميص فقد وجد تكون طبقة سميكة وصلبة و شديدة الالتصاق بالسطح مما تقلل من الفقد. فالفقد في كلا من خط انابيب الخلايا سابقة التحميص وخط انابيب الالومينا الخام يكون مهماً بالمقارنة بخط أنابيب الخلايا ذاتية التحميص حيث تكون النسبة 0.5 مم/سنة مقابل 5مم/سنة رغم تشابه ظروف الصدم من سرعة وحجم و نسبة تحميل الحبيبات،لذا فإن آلية التآكل في خطوط أنابيب الخلايا ذاتية التحميص هي تآكل ميكانيكي- كهروكيميائي.