COKE SELECTION CRITERIA FOR ABRASION RESISTANT GRAPHITIZED CATHODES

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Abstract

The high abrasion rate of graphitized cathodes of high amperage cells is a major limitation of the pot lining life time. This is related to the use of low Sulfur anode grade petroleum coke resulting in a too soft cathode after graphitization. A review of the effects of the coke characteristics on the cathode abrasion as well as other pot lining relevant properties has been performed in a pilot scale. The selection of more isotropic calcined cokes produced in a delayed coking plant from appropriate soft pitches allows a decrease in the abrasion rate by a factor of four. No detrimental effects on the graphitization behaviour or the cathode relevant properties can be observed. Dedicated coal tar pitch feedstocks used in optimized delayed coking in combination with shaft kiln calcination have the potential, to solve the "W shaped" wear of graphitized cathodes that is responsible for the short pot life time.

Introduction

In an excellent overview paper published in 1989 W.R. Hale [1] stated that by measuring the erosion rate of the cathode in the pot and knowing the thickness of the collector bars, plants can determine their ultimate pot life. However, he observed that few cathodes failed due to erosion on a regular basis.

One decade later cathode wear became the life-determining factor for high amperage pots boosted to high current densities [2]. The maximum erosion area systematically observed at the graphitized block ends, the so-called "W shape" erosion, was responsible for that significant reduction of the pot life time [3]. For high intensity / high current density pots the bench mark figure of 3000 days for semi-graphitic (30% Graphite) blocks was suddenly reduced to less than 2000 days when graphitized blocks were used.

As the current density is mainly driving the erosion process, different solutions have been studied to obtain a more homogeneous current distribution at the cathode block surface. Dreyfus and Joncourt [4] promoted the manufacture of blocks showing a high anisotropy factor of the block resistivity and later Dreyfus et al. [5] introduced the concept of variable resistivity cathodes for fighting the local W shaped graphite erosion.

These interesting approaches, however, were not economically successful, as a significant anisotropy of the extruded blocks required expensive needle like coke materials. A variable resistivity through adapted graphitization conditions means that a significant part of the block has an electrical behaviour similar to inferior, cheaper graphitic grade blocks.

Therefore an improvement of the cathode material is urgently needed to improve the resistance to the wear. A considerable amount of work on cathode characterization has been performed especially on the wear behaviour over the last two decades. Recently Skybakmoen et al. [6] concluded that the exact mechanism behind the "W" shaped wear pattern can still not be explained by the available laboratory test methods applied to different sophisticated laboratory cells. On top of this they confirmed that the laboratory cell set-ups, described in their excellent overview paper, were not able to distinguish between cathodes having different levels of apparent density. However, clear indications in the industrial practice exist that denser graphitized cathode blocks show a slower wear rate.

The shortest and best summary of the mechanisms at work is still given by Øye and Welch [2]. The chemical wear through Al_4C_3 formation as well as the physical wear, either by detachment of carbon or Al_4C_3, are operative mechanisms. The chemical wear is non-discriminating with regard to materials but depends on current density and electrolyte composition while the physical wear can be explained by the variable behaviour of different cathode materials.

Therefore we took, as a wear ranking criteria of cathodes, the physical abrasion measured on cathode disk specimens rotated with a given pressure on a sand paper surface. The test results overestimate the difference between graphitized and amorphous cathode erosion rate [7] but this physical abrasion sand paper test is a precise and very discriminating tool for judging the merit of any graphitized cathode type.

It is known that the hardness of graphitized cathode depends on the following parameters:

- Type and quality of coke
- Pitching level
- Mixing and forming intensities
- Impregnation
- Graphitization degree

In the studies reported below a fixed pilot plant manufacture of unimpregnated graphitized cathodes were used for investigating the impact of the type of coke, at their optimum pitch content, on the cathode relevant properties.

Selection of Cokes

Classical raw materials for graphitized cathodes have been tested in order to establish a base line of the graphitized cathode types currently available in the market. This included

- low Sulfur, low Vanadium anode grade petroleum coke,
- delayed pitch coke out of low QI tar,
- low Sulfur petroleum shot coke.

For petroleum coke the following candidates were considered:

- needle coke from decant oil,
- medium Sulfur, Vanadium anode grade coke,
- shaft kiln low Sulfur, Vanadium anode grade coke,

to cover first, the entire scale of the macrostructure (anisotropic needle coke), second the possible positive effect of the less anisotropic medium S/V coke and third of the harder shaft kiln coke related to the nature of the calcining process.

From the pitch coke family a second type of material, produced from a tar rich in high molecular weight component (high QI content tar) was selected as it is known and proven [8] that thanks to a more isotropic coke texture harder cathodes can be obtained.

In the same line, a medium temperature tar pitch coke (a by-product of coal gasification) was also selected. This material is unsuitable for use in prebaked anodes as brittleness, related to high coefficient of thermal expansion and inelasticity was experienced. These two cokes can be named as follows:

- delayed pitch coke out of high QI tar,
- medium temperature coal tar delayed pitch coke.

A low porosity isotropic coke produced out of oil shale residue by delayed coking was evaluated as well. An acetylene coke resulting from the agglomeration of carbon blacks during the preparation of acetylene through the partial combustion of methane was also tested. These two more exotic cokes, that are however produced on a significant production scale, can be named as follows:

- delayed oil shale shaft kiln calcined coke,
- calcined acetylene coke.

The 10 selected cokes were industrially calcined materials, most of them in rotary kiln except for the shaft kiln anode grade coke and the oil shale coke. The calcining degree was of course high for the needle coke, a normal practice for this type of material, and for the two low and high QI coal tar delayed pitch cokes. The other cokes were calcined at a typical degree for anode grade or for recarburizer materials.

Experimental

Graphitized Cathode Pilot Preparation

The calcined cokes were sieved in seven fractions from +8mm to -0.25mm. The oversize +8mm was crushed to -8mm and resieved. The finest fraction -0.25mm was blended with the intermediate material 1-0.25mm for the preparation of fines (3500 Blaine) using an air jet collision mill equipped with a classifier. The following dry aggregate recipe was used

8-4mm	14%	1-0.25mm	14%
4-2mm	14%	0.5-0.25mm	14%
2-1mm	14%	Fines 3500 Blaine	30%

An addition of 0.5% Fe_2O_3 fines was chosen for moderating any puffing tendency during the graphitization process.
A coal tar pitch with a medium QI content of 9% and a typical softening point (SP) Mettler of 112°C was used as a binder. The dry aggregates were preheated at 200°C prior to mixing.

An intensive impeller mixer (10 l, Eirich) was used. The paste temperature was adjusted to 182°C (70°C higher than the pitch SP).

For each coke the pitch content was varied in a 4% range which was selected according to the porosity characteristics measured on the coke.

For each pitching two batches of paste were produced and two pilot electrodes of 146 mm diameter and ~200 mm height were pressed with 200 bar at 140°C. The paste was cooled by using water injection into the mixer at the end of the mixing process.

Green pilot electrodes of 5 to 6 kg were baked in an electrical furnace at a rate of 10°C/h during devolatilization between 200 and 600°C. The soaking time was 20 hours at 1100°C.

Graphitizing was performed on three cores of 50mm diameter and 130mm length in a 100kW length wise pilot furnace where samples are pressed pneumatically at 10 bar pressure (Figure 1).

Figure 1. Length wise graphitization furnace for Ø50mm cores

The electrical current was adjusted in the range of 600 to 3000°C for maintaining a constant heat-up rate of 500°C/h. The length of the sample column was continuously registered in order to quantify the puffing pattern but also any post baking temperature shrinkage and / or graphitization shrinkage occurring at temperatures above 2000°C.

Testing

The calcined cokes were analyzed by using the classical routine quality control ISO standards. Additionally the porosity was measured by Hg pressure porosimetry and the Nitrogen content by gas chromatography after combustion.

The hardness of the coke, an important property of the calcined material revealing its macrostructure, was characterized by using the Hardgrove mill with increased number of revolutions (200 instead of 60 in the HGI ASTM D409 standard) and calculating the number of grams per minute of milling passing 75 Mesh [9]. This is reported as a pulverizing factor that is close to 1 for anode grade coke but can reach four times lower values for hard coke.

On the baked pilot anodes the sticking propensity of the packing material and the shrinkage of the pieces after baking were measured in order to detect optimum pitching conditions. Non-destructive testing were performed including the specific electrical resistance and the dynamic elasticity modulus that are also excellent indicators for optimum binder content for the graphitization stage.

On the dilatometric curves during the graphitization, the rate and the total extent of puffing, of post baking or post puffing shrinkage and graphitization shrinkage (T>2000°C) were determined.

The volumetric change on the cold samples (before and after graphitization) as well as the graphitization weight loss were measured.

On the graphitized cores beside the physical/thermal/electrical properties, the following tests relevant for the cathode behavior in the pots were performed:

- abrasion sand paper test (RDC-191),
- Rapoport swelling test (ISO 15379-1),
- sodium vapour test (RDC-193).

Results

Table I gives an overview of the data obtained for optimally pitched dry aggregates for which the corresponding graphitized cathode abrasion resistance was reached with the lowest possible level. The results of the coke candidates are ranked from left to right of the Table I in descending abrasion rates of the graphitized cathodes (see also Figure 2). It is interesting to note that the first five cokes with high abrasion rates are petroleum cokes, from needle to shot coke, followed by pitch cokes from coal process.

Then the shale oil shaft kiln coke and especially the coke by-product from the acetylene preparation process reached an unprecedented low abrasion rate which is six times lower than for graphite electrodes made with typical cathode raw materials.

Table I. Coke, baked and graphitized cathode results

	Source	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	Coal	Coal	Coal	Oil Shale	Acetylene
	Feedstock	Decant Oil	Low S Res.	M. S Resid	Low S Res.	High Asph.	Low QI	High QI	Med. T. Tar	Resid	-
	Calcination	Rotary	Rotary	Rotary	Shaft	Rotary	Rotary	Rotary	Rotary	Shaft	Rotary
	Grade	Needle	Anode	Anode	Anode	Shot	Cathode	Cathode	Recarb.	Recarb.	Recarb.
COKE PROPERTIES											
Sulphur	%	0.37	1.02	1.96	0.37	1.09	0.35	0.26	0.16	0.40	0.02
Nitrogen	%	0.28	1.04	0.96	1.66	1.42	1.18	1.40	1.50	0.30	0.30
Vanadium	ppm	1	35	194	7	482	13	10	1	1	8
Pulverizing factor	-	1.38	1.29	1.14	0.75	0.56	0.53	0.35	0.35	0.25	0.40
Density in xylene	kg/dm³	2.133	2.073	2.063	2.069	2.053	2.071	2.050	1.988	2.029	1.909
Crystallite size Lc	Å	35.1	28.0	28.1	26.6	26.2	35.7	38.8	27.3	23.3	19.4
Tapped bulk density 2-1mm	kg/dm³	0.901	0.862	0.794	0.926	1.087	1.010	1.042	1.064	0.980	0.971
Hg porosity	%	16.2	20.5	21.5	16.6	12.1	14.1	9.7	8.8	5.5	11.9
PITCH CONTENT		16%	16%	16%	14%	12%	14%	12%	12%	12%	10%
BAKED PILOT CATHODES											
Green apparent density	kg/dm³	1.716	1.648	1.600	1.651	1.628	1.655	1.671	1.661	1.645	1.552
Baked apparent density	kg/dm³	1.664	1.591	1.557	1.612	1.617	1.625	1.657	1.599	1.629	1.552
Baking loss	%	5.2	5.3	5.1	4.3	3.9	4.3	3.8	4.0	3.6	2.9
Shrinkage	%	2.2	1.9	2.5	2.2	3.3	2.0	3.0	0.3	2.6	2.8
Sticking of packing material	%	0.06	0.10	0.27	0.10	0.05	0.19	0.22	0.33	0.20	0.33
Sp. Electrical resistance	μΩm	62	59	59	62	46	48	43	43	53	59
Compressive strength	MPa	27.0	38.3	45.6	37.4	68.9	58.7	70.0	71.3	57.9	55.9
Dynamic elasticity modulus	MPa	5.8	7.8	8.3	6.6	10.1	9.3	10.3	9.8	8.5	9.6
GRAPHITIZATION BEHAVIOUR											
Puffing rate	$10^{-6}K^{-1}$	1.1	12.0	55.0	17.0	0.0	5.4	6.5	0.8	0.0	0.0
Post Baking Shrinkage rate	$10^{-6}K^{-1}$	0.7	0.8	0.0	0.0	4.1	2.1	0.9	10.7	32.9	40.8
Graph.Shrinkage rate	$10^{-6}K^{-1}$	18.3	17.1	13.2	14.6	12.2	6.1	2.8	18.1	0.0	0.0
Cold volumetric change	%	-1.56	-1.43	-1.53	-1.97	-5.58	-2.76	-1.80	-7.27	-3.97	-8.54
Graphitization loss	%	2.58	4.15	5.20	4.22	4.63	3.52	3.15	3.55	2.71	2.21
GRAPHITIZED CORES											
Graph. apparent density	kg/dm³	1.608	1.541	1.495	1.562	1.635	1.620	1.636	1.663	1.642	1.643
Sp. Electrical resistance	μΩm	14.0	13.7	16.7	16.3	10.7	13.3	14.7	13.3	14.7	34.7
Thermal conductivity	W/mK	86	87	84	78	99	93	98	98	83	37
CTE	$10^{-6}K^{-1}$	3.27	3.48	3.70	3.54	5.62	4.64	5.33	6.32	5.79	5.92
Xylene density	kg/dm³	2.245	2.235	2.226	2.236	2.213	2.198	2.171	2.171	2.205	2.081
Dynamic elasticity modulus	MPa	2.5	3.5	3.6	2.9	6.6	5.7	6.9	7.3	5.2	6.9
Abrasion	%	60	54	50	40	28	28	23	15	14	9
Compressive strength (CS)	MPa	12.0	15.9	20.4	16.9	37.4	32.2	42.0	50.0	30.9	40.2
CS after Na vapour test	MPa	17.0	17.1	18.8	23.5	24.4	31.7	26.2	29.9	30.6	14.4
Rapoport swelling	%	0.25	0.24	0.24	0.25	0.42	0.34	0.45	0.44	0.36	0.52

This shows how important the selection of the coke material is but also takes into account the behavior during the graphitization step and also the other relevant cathode properties.
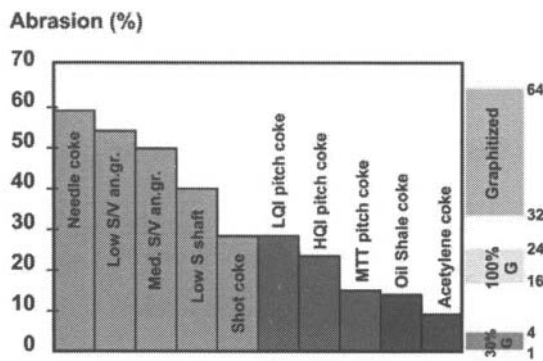
Abrasion (%)

Figure 2. Abrasion of pilot and range of production cathodes

Discussion

Petroleum Cokes

Dense petroleum cokes with low pitch requirement during the electrode manufacturing generally provide high density and abrasion resistant end-products. However, there are other aspects related to the coke macrostructure that appear to be more important for the cathode abrasion.

The anisotropic macrostructure of the needle coke resulted in a relative low strength, elastic and low CTE graphitized end-product with the highest rate of abrasion despite its high apparent density. On the contrary the relative isotropic macrostructure of the shot cokes produced out of a residue, rich in asphaltene, gives a higher strength, inelastic and high CTE graphitized cathode with a much lower abrasion value of 28% vs. 60% for the needle coke electrode.

The impact of the feedstock aromaticity and of the asphaltene content can be noticed among the classical anode grade coke calcined in rotary kilns. A higher Sulfur / Vanadium coke shows also a slight positive effect on the abrasion resistance of the cathode.

The positive effect of the slow shaft calcining process, related to the coking of evolved tars from the green coke on the coke pores, is also quite significant. Compared to the other low S anode grade coke calcined in rotary kilns, which has the same macrostructure characteristics (same CTE and Xylene density of the graphitized cathode), the abrasion value improves from 54% down to 40%.

The best indicator among the coke properties for predicting the abrasion level is the pulverizing factor. It integrates the micro-strength pattern resulting from the macrostructure of the coke or from the peculiarities of the calcination process, and this even though there is an intermediate graphitization step that might change the picture. Concerning this aspect, Figure 3 shows the dilatometric curves registered during the graphitization of the needle coke, low S anode grade and shot petroleum coke baked artifacts.

The puffing tendency of the low S/V anode grade coke is totally suppressed for the shot coke material though the S+N contents are quite comparable. There is massive post baking (>1100°C)

skrinkage up to 2100°C followed by pre-graphitization shrinkage up to 2700°C. But on the contrary to the needle coke material there is no end-graphitization shrinkage up to 3000°C, a sign that the shot coke is harder to be graphitized. As a consequence the level of the xylene density of the end product is significantly lower than for the graphitized needle coke artifacts (2.213 vs. 2.245 kg/dm^3). The suppression of the puffing for isotropic material along with the continuous shrinkage tendency during the graphitization (despite the high thermal expansion level) results, for the shot coke artifacts, in a volumetric change of the cold specimen after graphitization of -5.6% i.e. three times the values of the other tested petroleum cokes. This graphitization behavior is also favorable for a high resistance to the abrasion of the graphitized cathode but also for a low resistivity level.
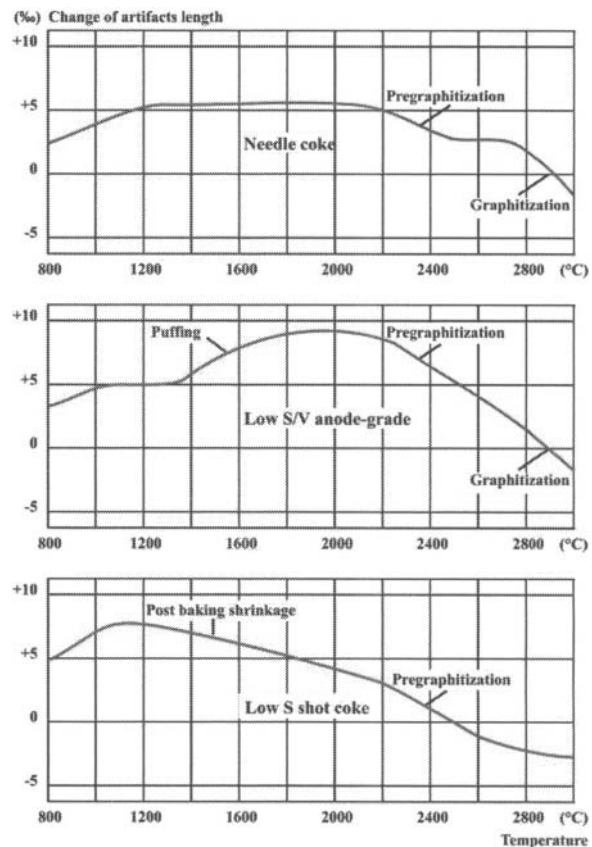

Figure 3. Graphitization dilatometric curves of pet cokes

Pitch Cokes from Coal Process

The level of abrasion of the low QI coal for pitch coke cathode is close to the one observed for the shot petroleum coke material. This is in line with the level of the pulverizing factor of the cokes though their different behaviour during graphitization. Figure 4 shows that there is a smaller post baking shrinkage from 1200°C to 1600°C followed by an expansion up to 2100°C where a moderate pregraphitization shrinkage process starts up to 3000°C.

The high QI coal tar pitch coke with a poorer graphitizability reflected by the lower xylene density of the graphitized artifact reaches only 2.17 kg/dm^3. The abrasion value is correspondingly lower (23 vs. 28%); a fact in line with the lower pulverizing factor of this pitch coke as well as its higher CTE (5.3 vs. 4.6•10^{-6}K^{-1} for the graphitized artifacts).

These results are in line with those reported in [8], the presence of high molecular weight components in the pitch feedstock hindering the formation of mesophase during coking. A harder fine mosaic pitch coke results from this selection of high QI tar prior to the soft pitch preparation process.
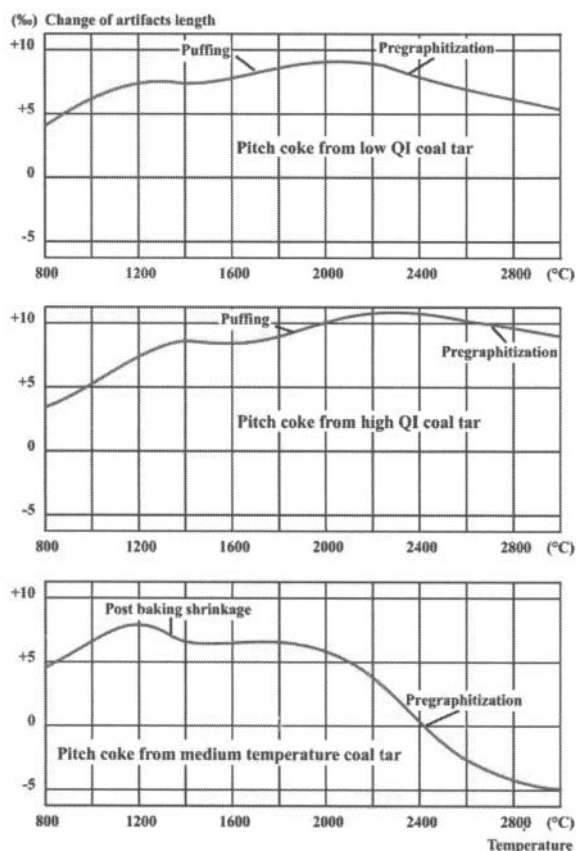

Figure 4. Graphitization dilatometric curves of pitch cokes

The medium temperature tar pitch coke results in interesting low cathode abrasion levels (~15%). This pitch coke shows the same low level of pulverizing factor as the high QI coal tar pitch coke but a more severe post baking shrinkage, no puffing tendency followed by a pronounced pregraphitization shrinkage from 2100°C to 2700°C. The CTE reaches the highest level $(6.3 \cdot 10^{-6} K^{-1})$ of the graphitized artifacts along with the highest levels of mechanical characteristics. This is related also to the massive volumetric change of -7% observed on the cold graphitized samples after the graphitization step.

Compared to more classical coal tar pitch cokes this material is more isotropic as its content in heteroatom (N,O) is higher due to the lower severity of the thermal treatment producing the tars (700°C in coal gasification process vs. 1100°C in the coke oven producing coal tar by-products).

Oil shale coke

The oil shale coke shows the lowest pulverizing factor but S/N levels close to be needle coke material. As shown in Figure 5 there is no puffing tendency but instead a strong post-baking shrinkage up to 1600°C followed by a plateau area up to 3000°C where the residual shrinkage compensates the thermal expansion. On the cold specimen the volumetric change is moderate (~ -4%).

Despite the high CTE value, the graphitized artifacts show a relative high real density level (2.205 kg/dm^3) comparable to the shot coke or to the low QI pitch coke materials. This is the sign of a reasonable level of graphitability confirmed by the moderate levels of the mechanical characteristics. However with the intrinsic hardness of this oil shale coke the abrasion rate of the graphitized artifacts (14%) is as low as for the best pitch coke tested here.
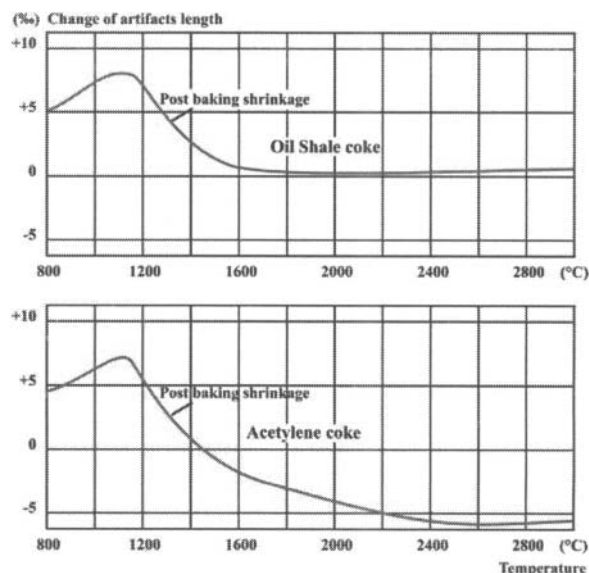

Figure 5. Graphitization curves of shale oil and acetylene cokes

Acetylene coke

The acetylene coke is a unique material having a low porosity that is mainly to be found in between the small carbon black like agglomerated particles. Its remarkably low level of real density (1.909 kg/dm^3) demonstrates its resistance to the heat treatment, which is confirmed also after the graphitization (2.081 kg/dm^3).

The pitch demand is extremely low (10%) and the level of apparent density unchanged after baking followed by an impressive increase after graphitization results from the massive post baking shrinkage (Figure 5) up to 2500°C.

The abrasion value reaches here an unprecedented one digit number of 8% which is six times better than for low S anode-grade coke and still three to four times lower than for shot petroleum coke cathodes. The drawbacks of this material are of course its poor level of electrical and thermal conductivities which is two to three times lower than typical. This is related to the nonplanar structure of the aromatic compounds [10].

Other cathode relevant properties

The cathode relevant properties for selected cokes are summarized in Table II and compared to the typical value of industrial cathodes. Even though there is a scale up factor between the pilot and the industrial scale it appears that the first three candidates gave results falling mostly in the typical range of graphitized industrial cathodes. This is not the case for the

- high QI coal tar pitch coke,
- medium temperature tar pitch coke,
- oil shale shaft kiln coke,

Table II. Cathode relevant properties: selected pilot plant and industrial cores data

	Source	Petroleum	Petroleum	Coal	Coal	Coal	Oil Shale	Acetylene	Vertical cores taken in industrial cathodes			
	Feedstock	Low S Resid	High Asph.	Low QI	High QI	Med. T. Tar	Resid	-	Graphitized	Graph. Impregn.	100 % Graph.	30% Graph.
	Calcination	Rotary	Rotary	Rotary	Rotary	Rotary	Shaft	Rotary				
Abrasion	%	54	28	28	23	15	14	9	32-64	30-40	16-24	1-4
Comp. Strength (CS)	MPa	15.9	37.4	32.2	42.0	50.0	30.9	40.2	15-34	25-40	20-34	22-38
CS after Na vapour	MPa	17.1	24.4	31.7	26.2	29.9	30.6	14.4	15-30	25-35	15-28	10-25
Rapoport swelling	%	0.24	0.42	0.34	0.45	0.44	0.36	0.52	0.1-0.4	0.1-0.3	0.4-0.5	0.5-0.8
Graph. apparent density	kg/dm^3	1.541	1.635	1.620	1.636	1.663	1.642	1.643	1.60-1.68	1.66-1.70	1.62-1.70	1.52-1.60
Sp. Electrical resistance	μΩm	13.7	10.7	13.3	14.7	13.3	14.7	34.7	10-14	8-10	18-24	30-48
Thermal conductivity	W/mK	87	99	93	98	98	83	37	80-110	100-120	25-40	7-13
CTE	10^{-6}K^{-1}	3.48	5.62	4.64	5.33	6.32	5.79	5.92	2.2-5.0	2.4-3.2	2.6-3.4	2.8-3.8

which gives better abrasion values together with compressive strength and CTE values on the high side or above the typical industrial range. The drawback of higher Rapoport swelling, observed here generally for the more isotropic coke cathodes, is not an issue as the swelling is still comparable to the graphitic cathodes that are known to be unproblematic for this aspect. The compressive strengths after the Na vapour test is also on the high side of the typical range, an indication that the cathode materials resist well to the sodium attack.

The higher CTE and Rapoport swelling might imply some adaptation on the cell lining geometry/design but the reduced abrasion, reaching the level of graphitic cathode, is a must for the pot life time.

Abrasion and Pot Lifetime

Impregnation, made industrially only on relative soft graphitized cathodes produced out of classical low S anode grade coke, has much lower potential of abrasion improvement than the one reached through an appropriate coke selection (Table II). Figure 6 gives the trend line for the average pot lifetime as a function of the abrasion of cathodes, as observed in several smelters [11].
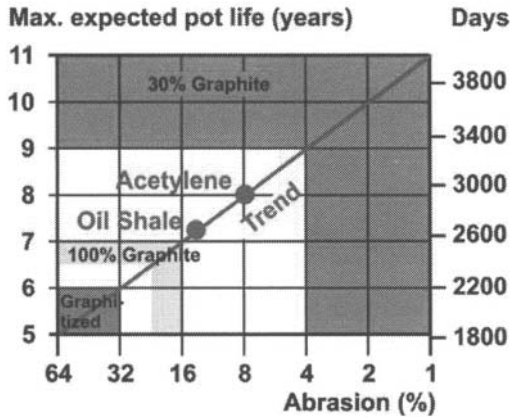

Figure 6. Potlife time vs. cathode abrasion

Oil shale and acetylene coke cathode showing abrasion values better than 100% graphite based cathodes (non-graphitized) and close to the level of the 30% graphite amorphous cathodes might improve significantly the potlife time by 1 to 2 years respectively.

Conclusion

The selection of relatively isotropic cokes allows a substantial improvement of the abrasion of the graphitized pilot artifacts.

There is a very promising potential especially in the delayed coking of soft pitches produced out of selected tars or out of soft pitches where the heavy molecular weight components are concentrated for the production of hard coke resulting in abrasion resistant graphite cathodes. This last route is quite attractive as it is complementary with the production of needle coke out of QI free soft pitch for the steel graphite electrodes.

In the same direction the growth of the bituminous sand processing for oil recovery can be an interesting option for preparing, by delayed coking of appropriate tars free of sand, a high potential coke for cathodes.

The option of blending of relative soft cokes with more exotic cokes, like the acetylene coke or others, can also be attractive for improving the wear resistance of the graphitized cathodes.

References

1. W.R. Hale, "improving the Useful Life of Aluminum Industry Cathodes", JOM, November 1989, pp. 20-25.

2. H.A. Øye and B.J. Welch, "Cathode Performance: The Influence of Design, Operations, and Operating Conditions", JOM, February 1998, pp. 18-23.

3. D. Lombard et al., "Aluminum Pechiney Experience with Graphitized Cathode Blocks", Light Metals 1998, pp. 653-658.

4. J.M. Dreyfuss and L. Joncourt, "Erosion Mechanisms in Smelters Equipped with Graphite Blocks", Light Metals 1999, pp. 199-206.

5. J.M. Dreyfus et al., "Variable Resistivity Cathode Against Erosion", Light Metals 2004, pp. 603-608.

6. E. Skybakmoen et al., "Laboratory Test Methods for Determining the Cathode Wear Mechanism in Aluminum Cells", Light Metals 2007, pp. 815-820.

7. H.A. Øye, "Carbon Cathode Materials Approval and Quality Control Procedures", Journal of Metals February 1995, pp. 14-19.

8. S. Toda and T. Wakasa, "Improvement of Abrasion Resistance of Graphitized Cathode Block for Aluminum Reduction Cells", Light Metals 2003, pp. 647-653.

9. R. Perruchoud and W. Fischer "Granular Carbon mechanical Properties" Light Metals 1992, pp. 695-700.

10. I.C. Lewis et al., "Conversion of petroleum feed stocks to coke", ACSDPC 1988, pp 404-412.

11. Private communications, 1995-2009.