

**High Vanadium Venezuelan Petroleum Coke,
A Rawmaterial for the Aluminum Industry?**

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The "Orinoco Oil Belt" in Venezuela is one of the largest oil deposits in the world. The special characteristic of this heavy oil is its high asphaltene and vanadium content. Together with the Venezuelan oil industry represented by INTEVEP, Swiss Aluminium Ltd. has conducted a joint research and development program, to investigate the influence of vanadium on the various steps in aluminum production. The interrelationship of petroleum coke quality, anode manufacture, cell performance and metal quality was investigated. The influence of high vanadium contents on aluminum and its alloys was studied in detail. The results obtained with a 500 ton heavy oil coke sample, produced in a specially designed delayed coker pilot plant in Venezuela indicate that high vanadium coke anodes can be produced which are suitable for use in the reduction process.

INTRODUCTION

The "Orinoco Oil Belt" in Venezuela is one of the largest oil deposits in the world. The special characteristic of this heavy and very dense crude is its high asphaltene, sulfur and vanadium content. Delayed coking is a proven commercial process to upgrade this type of oil. Its application results in a good quality synthetic oil and petroleum coke which, however, contains a high vanadium content. Since the aluminum industry is one of the main customers of petroleum coke there appeared to be a need to carry out an investigation into the use of vanadium rich coke in the preparation of anodes for the aluminum industry. Such an investigation has been underway since 1982 in a joint effort between the Venezuelan oil industry, represented by its research center INTEVEP and the aluminum industry, represented by the R & D Division of Swiss Aluminium Ltd. This research includes:

- * Designing, constructing and operating a 250 BPD delayed coking pilot plant to produce 500 tons green coke from crude of the "Orinoco Oil Belt",
- * Calcining this green coke in a conventional calciner,
- * Determining anode and cell performance in a commercial operation and
- * Investigating the influence of vanadium on properties of aluminum and its alloys.

PRODUCTION OF HEAVY OIL PETROLEUM COKE.

Delayed coking

In order to produce 500 tons of green coke required for the research program a delayed coking pilot plant was designed and built with a capacity of processing 250 BPD of heavy crude, ranging from 8 to 20 degrees API with a daily production capacity of 5 tons green coke. This coking unit operates like a commercial delayed coker with a coke drum cycle of 48 hours. A detailed description of this coking unit has been given elsewhere (1).

Heavy oil green coke

The coke yield obtained from the heavy oil mainly depends on the type of residue and the recycle ratio used. For a 275 degree C plus residue and 1.5 recycle ratio the coke yield was about 22.5%. The main characteristic of the green coke produced is shown in table 1.

Characteristic		Standard coke	Heavy Oil coke
Bulk density	g/cm ³		0.602
Water content	wt %	5- 10	5- 10
Volatile matter	"	10- 14	11- 13
Ash	"	.2- .3	0.5
Fixed carbon	"	80	80.9
S	"	1.5- 4	4-4.5
Na	ppm	120-130	50- 80
Si	"	100-130	120-240
Fe	"	100-200	35- 55
Ti	"	10- 30	30
Ca	"	50-300	100-170
V	"	150-350	1500-2000
Ni	"	50-200	390-460

Table 1: Characteristic of green coke.

Compared to a typical standard green coke only the high impurity in vanadium and nickel are different in the heavy oil green coke.

Heavy Oil calcined coke

The 500 tons of green coke were calcined in a commercial type rotary kiln in the US. Based on standard practices, R&D Carbon Ltd., under contract from Swiss Aluminium Ltd., first performed a "Dynamic Calciner Optimisation" (DCO) to determine the best calcining condition (2). According to the results obtained during the DCO the heavy oil green coke can be calcined 60 ° C below normal calcination temperature. A normal coke yield of 72% was achieved and a desulfurization of 17% could be observed. The characteristic of this calcined coke is shown in table 2 below

Characteristic		Standard coke	Heavy Oil coke
Real density	g/cm ³	2.05-2.09	2.00
Bulk density	"	0.74-0.80	0.90
CO ₂ reactivity	%	5 - 10	4
Air reactivity	%/min	0.10-0.20	1.50
Sp.el.resist.	μΩm	520 - 480	680
S	%	1 - 2.5	3.90
Na	ppm	30 - 90	80
Si	"	50 - 250	240
Fe	"	50 - 250	210
Ti	"	1 - 5	15
Cr	"	1 - 10	50
V	"	80 - 160	2280
Ni	"	50 - 160	530

Table 2: Characteristic of calcined heavy coke

Compared to a standard coke, the Venezuelan heavy oil coke shows some basic differences. It is a very isotropic, low real density, high resistivity coke which has excellent CO₂ reactivity but a poor air reactivity. The impurity level is, as expected, high in vanadium, nickel and sulfur.

ANODE MANUFACTURE

Recipe optimisation

Since the properties of the calcined heavy coke considerably differ in several aspects from standard coke, an intensive recipe optimisation was required. In the first test series the following variations were made:

Pitch content	13	14	15	16	%
Dust fraction	24	30	36	42	%
Alumina addition	0	2	4	6	%

A total of 12 anodes with different recipes were produced and tested in a reduction cell. Of these 12 anodes 11 cracked immediately after introduction into the pot due to thermal shock. Only the anode with a high dust (42%) and low pitch content (15%) did not crack. In order to reduce the apparent density and to lower the bending strength, some production parameters such as mixing intensity and moulding pressure were modified. Another 12 anodes with 13% pitch and 42% dust were produced and set again in the reduction cell. Out of these 12 anodes again 11 suffered severe thermal shock damage. The results of the two test series led to the conclusion that the

production of thermo-shock free anodes from pure heavy oil petroleum coke is not possible. Only a drastic change in the process parameters of the delayed coking unit could result in a coke quality with acceptable properties for anode manufacture.

The third phase of anode recipe optimisation was therefore performed with a mixture of 50% heavy oil coke and 50% standard petroleum coke. Again dust and pitch content were varied. The following recipe variations were made:

- Recipe 1: 50% standard coke
50% heavy oil coke in the grain fraction and dust.
15% pitch
- Recipe 2: same as recipe 1 except
16% pitch
- Recipe 3: 50% standard coke, all in the dust fraction
50% heavy oil coke only in the grain fraction
15% pitch
- Recipe 4: same as recipe 3 except 16% pitch.

From the four different recipes 3 anodes each were produced and tested in 12 different reduction cells. The results in term of thermal shock were as follows:

- Recipe 1: no anodes cracked
- Recipe 2: 1 anode cracked
2 anodes did not crack
- Recipe 3: 1 anode cracked
2 anodes did not crack
- Recipe 4: all anodes cracked

A repetition of this test gave similar results, i.e. thermo-shock free anodes can only be produced using 50% standard coke and 50% heavy oil coke in the grain and dust fraction with a pitch content of 15%.

Anode quality

Based on the results gained from the described process optimisation a total of 517 anodes were produced. The anode quality is shown in table 3.

Characteristic		Standard coke	Heavy coke
Appar.density	g/cm ³	1.53-1.58	1.61
Real density	"	2.05-2.08	2.04
Spec.el.res.	μΩm	52- 62	50
Flex.strength	105N/m ²	80- 120	105
Compres.str.	" "	320- 480	549
Elast.module	108 "	40- 60	65
Therm.cond.	W/mK	3.00-4.00	4.67
Air perm.	nPm	0.50-1.50	0.50
CO ₂ reactivity	%	80.0-85.0	88.1
Air reactivity	%		75.8
S	%	1.20-2.40	1.73
Na	ppm	400-1000	465
Fe	"	100- 500	618
V	"	80- 260	772
Ni	"	80- 160	235

Table 3:Characteristic of heavy coke anode

The main difference compared with anodes made from standard petroleum coke are, besides the high vanadium and nickel impurity level, the high apparent density, high

thermal conductivity, compressive strength and elasticity and the excellent CO₂ reactivity. All other values are more or less in the range of a standard anode quality.

INFLUENCE OF HIGH VANADIUM ON POT PERFORMANCE

Preliminary tests

One of the major objectives of the heavy oil coke utilisation program is to measure quantitatively the impact of using anodes in commercial aluminum cells. As there was no previous experience with such an unconventional coke the investigation was carried out in various phases.

In phase 1 a heavy oil petroleum coke with 330 ppm of vanadium was chosen as a first approach. The results of this test were reported at the AIME 1985 (3) and can be summarized as follows:

Tests were carried out in seven 45'000 Amp. cells over seven months. 95 pots with standard anodes served as reference. The main operational results are shown in table 4.

		Test pots Jul./Dec.	Normal pots Jul./Dec.84
Pot voltage	V	4.54	4.60
Current eff.	%	87.9	88.7
Energy cons.	kWh/kg	15.40	15.45
Anode cons. gross	gC/kg	499.5	502.9
net	"	435.1	428.0

Table 4: Operating results of test pots with 390 ppm V in anodes compared to pots with standard anodes.

The results obtained in this first phase show that the increase in vanadium from 120 to 390 ppm caused the current efficiency to decline by 0.5-1% and the non electrolytic anode consumption to increase by approx. 7%. The vanadium content in the metal increased as expected from 70 to 170 ppm.

Main electrolysis test with Venezuelan heavy oil coke anodes.

A large scale test which will last six months has been underway since July 1988. Anodes manufactured as described above, i.e. a mixture of 50% heavy oil coke with 50% standard coke are being tested and compared with standard anodes. The production parameters are:

No. of test pots		3
No. of anodes per pot		22
Anode cycle	days	30
Alumina coverage	cm	10-15
Current intensity	KA	87

Table 5: Production parameters of test pots

After two months operation the results achieved can be summarized as follows:

- All test pots are running smoothly
- No thermal shock was observed
- No extreme air burn occurred (due to good alumina coverage)

- The vanadium content increased from 70 to approx. 350 ppm.

The period of two months operation is too short to present figures on pot performance. The final results will, therefore, be reported at the presentation of this paper during the forthcoming 1989 AIME meeting.

METALLURGICAL ASPECTS OF VANADIUM IN ALUMINUM AND ITS ALLOYS.

General information.

A sharp increase in the vanadium content of primary aluminum would not go unheeded by the aluminum processing industry or by the users of aluminum. For that reason various investigations have been made to determine what measures would be necessary with various products and what benefits might be attainable from the presence of an increased level of vanadium in the metal. In this paper only a few aspects can be highlighted to put the matter into perspective. More detailed results have (4) and will be published elsewhere.

Vanadium in aluminum melts.

As a first point of orientation it should be mentioned that in pure aluminum the melt is capable of sustaining 1000 ppm vanadium at the freezing point without forming primary particles. As the Al-V system at the Al end features a peritectic reaction, just below the freezing point, the metal should be capable of holding up to 3700 ppm of V in solution. Under normal casting conditions, however, the peritectic reaction is not encountered and any increase in solid solubility of V above 0.1 % is achieved by non-equilibrium cooling of the melt. The critical V content at which coarse primary particles will form in the melt depends, therefore, both on the presence of other elements e.g. Mn and Cr and on the casting conditions. Relationships of the mutual compatibility of elements in this respect have been established (5) so that it is possible to determine the acceptable levels of these elements.

In high strength alloys it has been found (6) that the V can also be substituted for some of these additions without any loss in properties. Along with good foundry practices up to 500 ppm V should present no problems in that direction. At 1000 ppm more care and possibly substitution of elements may be necessary in certain high strength alloys.

In conductor grade material the concentration of V + Zr + Cr + Mn may normally not exceed 300 ppm, and so precipitation of the first three elements by boron treatment of the melt is standard practice. If necessary V can be completely removed by that method.

Vanadium in Aluminum and its Alloys

Vanadium is a relatively expensive additive to aluminum and so its use as an alloying element has not had a high priority in the industry. The metallurgical investigations made in connection with this work have shown, however, that there are various benefits to be obtained with the addition of this element. A study of the AlMgSi system (4) revealed that the main influence of V is to promote the formation of the cubic α -phase $Al_{12}(FeMn)_3Si$ during homogenisation. As a result a smaller grain size is obtained on solution treatment and the structure is more resistant to over heating.

Similarly in extrusions and forgings the fine grain structure enables cold forming to be performed without risk of the orange peel effect. Another consequence of the increase in the density of α -phase particles is that the colour tone of clear anodized sheet can be influenced (6). This effect, however, is noticeable only if sufficient manganese is also present to boost the influence of V. By appropriate choice of composition and heat treatment the influence can be eliminated or exploited as required.

The same mechanism, viz., an increase in the number of grain boundary pinning α -phase particles, is presumably partly responsible for the effectiveness of V in the standard alloy AA2219, which offers resistance softening at elevated temperature. More recently (7) this has been exploited to a greater extent by high supersaturation of V via rapid solidification and subsequent dense precipitation of the α -phase. Such V-containing alloys out-perform other developments in that direction and hold considerable promise. Also it had been shown (6) that although vanadium inhibits recrystallisation, the addition of 500 ppm V to can body stock AA3004 does not produce any increase in 45 degree earing; the presence of 1000 ppm V on the other hand produces a slight increase (0.5-1%) in earing but a parallel increase in strength. The normal measures to counter earing are considered adequate to meet product requirements also in the latter case.

Finally it can be said that the major problems arising from an increase in the V content of aluminum and its alloys are limited and known. Sometimes an apparently negative influence can be turned to advantage. So for example the increase in electrical resistivity due to vanadium can be used to improve the ease and economics of spot welding. (8)

Also, as the mechanisms by which V influences properties are known, it should be easier to manage such metal and to derive further benefits from it. If necessary, the primary metal industry could remove the vanadium completely by boron treatment. This, however, would be costly, unnecessary and even withhold potential benefits for the user. The economics of melt treatment depend on the fraction of metal which would require treatment. This aspect merits separate in-depth investigations and will not be entered into here. For the present it can be said that a scenario of that kind is technically and economically feasible.

OUTLOOK AND CONCLUSION

Outlook on Vanadium concentration in Petroleum coke

For our project Pace Consultants Inc. have calculated the petroleum coke production in the major world regions for 1979 through 1998 (9). This information was developed using Pace's historical data base for petroleum coke and quality, plus history and forecast of crude oil production and the expected coke feedstocks for existing, planned and anticipated coker expansions. A summary of the results is given in Table 6 below.

Region	Vanadium content in ppm				
	1979	1983	1988	1993	1998
United States	225	451	635	665	665
Canada+Mexico	502	576	597	587	587
South America	46	41	51	335	335
Western Europe	110	117	138	177	177
Middle East	350	384	382	286	286
WWA*	210	404	553	579	694

* Western World Average

Table 6a: Development of Vanadium content in Petroleum coke 1979 - 1998

Region	Pet coke prod.1000 sht/d				
	1979	1983	1988	1993	1998
United States	36.3	49.0	64.3	72.0	72.0
Canada+Mexico	1.1	4.1	4.1	4.2	4.2
South America	2.2	3.2	3.5	5.2	5.2
Western Europe	5.0	5.2	6.2	6.8	6.8
Middle East	0.6	0.9	0.9	2.7	2.7
WWA tot sht/d	46.3	63.2	80.7	93.6	120*
mio mt/y	15.3	20.9	26.7	31.0	39.8

* Including anticipated expansions of 26'500 sht/d

Table 6b: Petroleum coke production in the Western World 1979-1998.

The quality of total petroleum coke produced in the Western World (WW) is based on the weighted average quality of all the above regions. Important points to note regarding this quality are as follows:

- * As would be expected, United States production dominates the quality of petroleum coke production. This trend will continue in the future.
- * Vanadium content of petroleum coke produced in the WW has more than doubled since 1979. It is currently over 500 ppm. In the same period, the volume of petroleum coke rose by 34'000 short tons per day - an increase of over 75 percent.
- * While the quantity of petroleum coke between 1988 and 1993 is projected to increase by over 16 percent, reaching approximately 94'000 short tons per day, the vanadium levels in petroleum coke will rise from 553 to 580 ppm. This slow increase in vanadium concentration is due to the domination of cokers existing in 1988. Between 1993 and 1998, petroleum coke production is expected to rise by

almost 30 percent. Incremental sources of this petroleum coke, as discussed above, will be primarily from crude oils with high vanadium content. This will cause the vanadium content of total petroleum coke produced in the WW to rise by over 100 ppm. The increase will be due almost entirely to this incremental rise, since we expect all other coke qualities to remain reasonably constant throughout the period.

* An additional point of interest regarding vanadium levels in world petroleum coke is the distribution of concentrations. As shown in table 7 below:

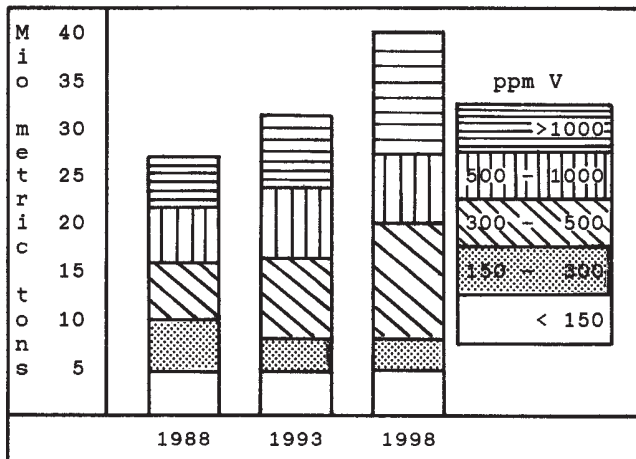


Table 7: Distribution of vanadium in pet coke

- * Very low vanadium content petroleum coke production in 1988 is approximately 5 million metric tons per year; there is no significant change in its total production over the time period.
- * The 150-300 ppm vanadium content category which is mainly considered anode grade calcined coke feedstock, is expected to drop from approximately 5 million metric tons per year to below 3 million metric tons.
- * Petroleum coke containing vanadium levels between 300-500 ppm is expected to register a sharp increase between 1989 - 1993 due to deterioration of existing coke quality (currently between 150-300 ppm) coupled with new expansions that will produce coke in this range. This increase remains strong between 1993 and 1998, representing approximately 5 million metric tons per year of production. The largest increase is expected between now and 1993.
- * Petroleum coke containing vanadium levels exceeding 1,000 ppm also represents approximately 5 million metric tons--or 20 percent--of production. The total volume is expected to rise somewhat between now and 1993. Between 1993 and 1998, petroleum coke with vanadium levels in this range will approximately double, due to processing of Mexican, Venezuelan, offshore California, and heavy Canadian crude oil.

Conclusions

Based on the Pace study on vanadium in petroleum coke and our own investigations on high vanadium petroleum coke utilization the following conclusions may be drawn:

1. The availability of petroleum coke for the aluminum industry is secure for the long term.
2. The amount of petroleum coke with a vanadium content below 300 ppm, which is today considered as acceptable anode grade coke will, however, decrease from 10 to below 8 million tons, over the next decade.
3. Since the need for anode grade petroleum coke will increase with the increase in the world aluminum production, anode grade coke with vanadium concentrations less than 300 ppm will become scarce and its price may rise.
4. As there is ample petroleum coke available with a vanadium content 300 - 500 ppm, this material will appear on the market and will have to be utilized partially for anode production. This means that the overall vanadium content in the anodes will increase and consequently also the vanadium content of the primary metal.
5. The results from our study have shown that high vanadium petroleum coke can be used for aluminum production. Even petroleum coke with very high vanadium content (>1000ppm) can be used as a raw-material for anode manufacture, if applied properly. Recipe optimisations will be necessary to achieve an anode quality which performs satisfactorily in the reduction process.
6. High vanadium anodes may have an influence on pot performance and anode consumption and certainly the vanadium content in the primary metal will increase.
7. Our extensive metallurgical research work has proven that the major problems arising from an increase in the vanadium content of aluminum and its alloys are limited and known. In many cases higher vanadium contents can even have a positive effect on the properties of aluminum and its products. There are however also negative aspects which may not be neglected. On the other hand there is always the possibility of removing vanadium from the melt where this is absolutely necessary.

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