

STUDIES OF THE IMPACT OF VANADIUM AND SODIUM ON THE AIR REACTIVITY OF COKE AND ANODES

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Abstract

Many significant studies have been published which examined the impact of vanadium and sodium on the air reactivity of cokes and anodes. Most studies have compared different cokes with differing levels of vanadium and sodium to make inferences about their impact on coke and anode quality. The studies discussed in this paper involve a single coke with different levels of vanadium and sodium (effectively holding other variables constant). Inferences drawn are therefore based on direct responses to the variables studied.

Reduced levels of vanadium were achieved by hydrotreating coker feedstock. Increased levels of vanadium were achieved by spiking coker feedstock with an organo-metallic vanadyl porphyrin compound. Sodium levels were effected in a variety of ways. Results indicate that vanadium has less impact on air reactivity than previously published and that sodium is approximately five times more leveraging than vanadium on both coke and anode air reactivity.

Introduction

Vanadium and sodium have long been known to catalyze oxidation of carbon, either in the form of calcined petroleum coke and/or anodes for the production of aluminum. The studies presented here are aimed at quantifying the impact on air reactivity rates of calcined coke and anodes as a function of each impurity. Three experiments are presented. First, a study of the effect on coke and anode air reactivity on a coke and subsequent anodes with baseline and elevated levels of vanadium. Second, a study of the effect on coke and anode air reactivity with baseline and reduced levels of vanadium. Third, a full factorial experiment examining low and high levels of both internal and surface sodium and reduced and baseline levels of vanadium (a confirming study).

Historical work in the area of coke and anode air reactivity has established that catalytic effects are functions of vanadium as well as many other coke properties such as structure (isotropy), surface area, porosity, and other chemical impurities such as sodium, sulfur, calcium, nickel, etc.⁽¹⁾⁽²⁾⁽³⁾. All literary references researched by the authors, compared air reactivity of cokes and anodes to differing levels

of vanadium. Without exception however, the cokes (and subsequent anodes) had other differences as well, such as feedstock, commercial or laboratory coking and calcining processes and plant/pilot plant equipment. Although extensive work has been done to characterize such differing cokes into families where variation of only one measured property occurred⁽²⁾, no study was found where all other properties, measured or not, were attempted to be held constant.

The unique set of laboratory capabilities at ARCO's Engineering and Technology Center afforded the opportunity to manufacture green coke at different vanadium levels while holding all other variables essentially constant. The coking, calcining, anode fabricating and baking process laboratories allowed a high degree of control over process variables for each of the processes. As such, we are confident that inferences drawn from the following experiments are not confounded by the inherent variability due to the processes, sample preparation or analytical techniques employed.

Pilot Plant Process Conditions

The pilot plant coker is operated under conditions which produce coke quality as close to normal refinery production as possible. The unit is run on a 14 hour, once through cycle at 5.5 MPa (40 psig) and 460°C (860°F). Batch calcination is carried out on 1 kg samples at 1225°C for 90 minutes and typically yields a real density of 2.060 g/cc. Anode fabrication uses a standard straight line granulometry, standard pitch at a concentration of 16.5% and without butts. Anode baking is standardized as follows: A heat up rate of 25°C/min from ambient to 300°C, then 10°C/min to 700°C, then 30°C/min to 1100°C followed by a 7 hr hold and then cooled at 25°C/min to ambient.

Analytical

Coke air reactivity is measured by the RDC-142 apparatus in %/min using a 10°C/min heat up rate (0.5°C/min unit was not available for some early experimentation). Sulfur is measured by XRF. Metals are measured by ICP. Anode air reactivity is measured by an isothermal, thermogravimetric technique at 550°C on 25mm X 25mm cylindrical cores.

Experiments

Experiment 1

The purpose of the first experiment was to determine the impact that elevated levels of vanadium would have on coke and anode air reactivity. The methodology was to spike the coker feedstock (heavy resid obtained from ARCO's Cherry Point Refinery) with a vanadium compound. Coke was then manufactured in a pilot plant coker, calcined in a batch calcination process and finally laboratory scale anodes were fabricated. Analytical and physical testing were performed on the cokes and anodes. The green and calcined coke test results can be viewed in Table 1. Anode results are presented in table 2.

Background research⁽⁴⁾ and analytical efforts determined that the most common vanadium compound found in Alaskan North Slope crude was Vanadyl (IV) meso-tetraphenylporphyrine (C₄₄N₄H₂₈VO, molecular wt.=679.61). This vanadyl compound was therefore selected to spike the vanadium content of the resid and coke. The resid was heated to approximately 150°C and the vanadyl compound was mixed in to spike the resid. The target calcined coke vanadium content was 550-600 ppm. The actual calcined coke vanadium content achieved was 570 ppm.

Experiment 2.

The purpose of the second experiment was to determine the impact that reduced levels vanadium would have on coke and anode air reactivity. The methodology of this experiment was to demetalize the identical coker feedstock as that of experiment 1. The sample of coker feedstock was catalytically demetalized at Pittsburgh Applied Research Center. The hydrotreating catalyst was chosen to preferentially demetalize rather than desulfurize the resid. The sample used in this experiment was hydrotreated at a high level of severity. It should be noted here that hydrotreating also removes sulfur, nickel, iron, silicon, calcium, sodium and other trace elements and effects physical properties such as porosity and vibrated bulk density. Therefore, inferences drawn regarding the impact of vanadium alone are less reliable than those of experiment 1. Baseline and demetalized coke quality properties are tabulated in table 3. Additionally, anodes manufactured from this coke had to be pitched at higher than standard levels to achieve optimum anode performance properties. Anode properties at both pitch levels are provided in table 4.

Experiment 3

The purpose of the third experiment was to evaluate the impact of both vanadium and sodium on coke and anode air reactivity and any interactions. Additionally, the experiment evaluated the effect of internal sodium (present in the resid prior to coking and therefore bound internal to the coke structure) vs external sodium (present on the surface of the coke). The experimental design was a full factorial with three variables at two levels. The variables were vanadium, internal sodium and external sodium. The respective levels were: vanadium, low=140 ppm (resid hydrotreated coke from experiment 2) and high=420 ppm (baseline), internal sodium,

low=26 ppm (baseline), high=226 ppm and external sodium, low=0 ppm (baseline) and high=100 ppm. The internal sodium high level was obtained by mixing an aqueous solution of sodium chloride to the resid prior to coking. The external sodium high level was achieved by soaking the green coke (from baseline coker runs) with a solution of sodium chloride and allowing the water to evaporate. Again, anodes were manufactured and anode reactivity measured. Coke and anode results from experiment 3 are presented in tables 5 and 6.

Table I. Green and Calcined Coke Properties Experiment 1

Property	Green and Calcined Coke	
	Baseline	Spiked
Green Coke		
VCM, %	9.9	10.5
HGI	68.2	62.4
Calcined Coke		
V, ppm	390	570
Air React %/min	.11	.23
Na, ppm	12	27
Ca, ppm	28	20
Ni, ppm	154	162
Fe, ppm	62	57
S, %	2.81	2.77
VBD (g/cc)	0.95	0.95

Table II. Anode Properties Experiment 1

Property	Anode Properties	
	Baseline	Spiked
BAD (g/cc)	1.54	1.55
ER (uOhmm)	67.9	63.9
Air React. (mg/cm ² hr)	41.8	69.9
Air React. Dusting (mg/cm ² hr)	6.0	10.5
CO ₂ React. (mg/cm ² hr)	3.5	3.6
CO ₂ React. Dusting (mg/cm ² hr)	5.1	4.8
TC (W/mK)	1.84	1.83

Table III. Calcined Coke Properties Experiment 2.

Property	Calcined Coke	
	Baseline	Demetalized
V, ppm	418	142
AR %/min.	0.14	0.04
Na, ppm	26	5
Ca, ppm	12	9
Ni, ppm	184	118
S, %	2.77	1.87
VBD (g/cc)	0.928	0.841

Table IV. Anode Properties Experiment 2

Properties	Anodes	
	16.5 % Pitch (Normal)	18.5 % Pitch (Optimum)
BAD (g/cc)	1.45	1.50
ER (uOhmm)	74.4	64.8
Air React. (mg/cm ² hr)	47.7	36.5
Air React Dust (mg/cm ² hr)	15.3	8.6
CO ₂ React. (mg/cm ² hr)	4.9	3.8
CO ₂ React Dust (mg/cm ² hr)	5.9	4.0
TC (W/mK)	1.33	1.45

Discussion of Results

Examination of the data from experiments 1 and 2 afford the following observations. The slope of coke air reactivity as a function of vanadium is very linear from the demetalized coke through the spiked coke as seen in figure 1. Experiment 1 suggests that a 100 ppm increase in vanadium would increase coke air reactivity by approximately 0.06 %/min. Experiment 2 suggests that a 100 ppm decrease in vanadium (as well as decreases in other metallic and sulfur contaminates) would decrease coke air reactivity by 0.04%/min. The combined slope of both experiments 1 & 2 suggests that a 100 ppm change in coke vanadium would change coke air reactivity by approximately 0.05%/min.

Table V. Calcined coke properties Experiment 3

Descript. (V-iNa-eNa)	ppm V, iNa, eNa	Air React. %/min
LLL	140, 26, 0	0.05
LLH	140, 26, 100	0.18
LHL	140, 226, 0	0.10
LHH	140, 226,100	0.22
HLL	420, 26, 0	0.15
HLH	420, 26, 100	0.27
HHL	420, 226, 0	0.15
HHH	420, 226, 100	0.25

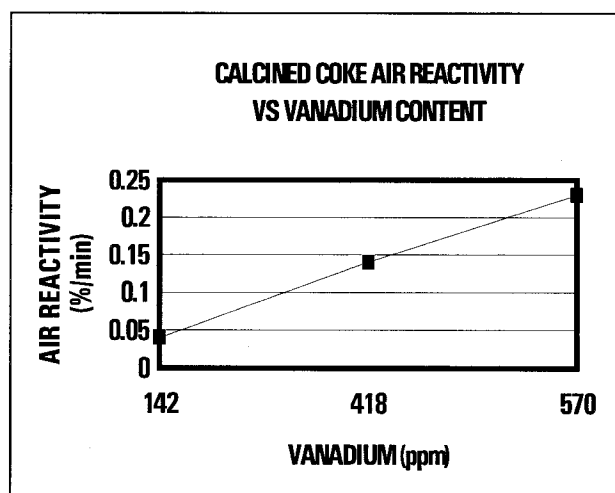


Figure 1. Calcined Coke Air Reactivity vs Vanadium

The results of experiments 1 and 2 also suggest that decreasing sulfur and metals other than vanadium have little effect on coke air reactivity over the range examined in experiment 2.

Statistical evaluation of the data in experiment 3 yields the following two regression equations for coke and anode air reactivity as a function of vanadium, internal sodium and external sodium:

$$CAR = 0.033975 + 0.000241 (V) + 0.000088 (iNa) + 0.001175 (eNa)$$

$$AAR = 26.8225 + 0.0509 (V) + 0.02125 (iNa) + 0.2675 (eNa)$$

Table VI. Anode Properties
Experiment 3.

	LLL	LLH	LHL	LHH	HLL	HLH	HHL	HHH
BAD (g/cc)	1.47	1.48	1.53	1.44	1.56	1.52	1.53	1.50
ER (uOhm m)	77.1	80.7	68.1	74.9	61.9	61.4	66.1	65.4
Air R.	29.8	67.9	35.7	66.4	45.6	76.2	62.7	72.0
Air R. Dust	3.2	33.7	6.0	32.0	4.3	13.4	17.3	14.9
CO ₂ R.	5.4	9.8	5.8	7.6	3.8	4.4	7.3	5.3
CO ₂ R. Dust	5.7	9.4	4.2	7.7	4.1	5.2	6.0	6.2
TC (W/mK)	1.62	1.55	2.08	1.91	1.74	1.66	1.50	1.04

CAR denotes coke air reactivity, AAR denotes anode air reactivity, iNa denotes internal sodium and eNa denotes external sodium. The linear correlation coefficients (r^2) of the above models are 0.92 for the coke air reactivity model and 0.80 for the anode air reactivity model.

The coke air reactivity model from experiment 3 supports the results of experiment 2. When the baseline and demetalized data from table 2 are plugged into equation 1, the predicted coke air reactivity is 0.07%/min for the demetalized coke and 0.14%/min for the baseline coke. The corresponding actual data from table 2 are 0.04 and 0.14%/min. This model predicts a 0.024%/min increase in coke air reactivity for a 100 ppm increase in vanadium from the demetalized coke and a 0.118%/min increase in reactivity for a 100 ppm increase in external sodium. The effect of external sodium on coke air reactivity is five times that of vanadium. Again the observations from experiment 2 indicated that a 100 ppm increase in vanadium would increase coke air reactivity by 0.04%/min.

Additional noteworthy findings indicate that External sodium is approximately 13 times more leveraging than internal sodium.

Conclusions

The three studies presented in this paper indicate that different levels of vanadium in essentially identical coke have the following effects: Increasing vanadium from a baseline of 390 to a spiked level of 570ppm increases coke air reactivity by 0.06%/min for every 100ppm increase in vanadium (experiment 1). Increasing vanadium from 142 ppm (demetalized) to a baseline of 418 ppm increases air reactivity by 0.04%/min (experiment 2). Experiment 3, which essentially repeated experiment 2 as a part of the factorial design, indicates that increasing vanadium from 140 ppm (demetalized) to 420 ppm, increases coke air reactivity by 0.024%/min.

The findings of experiment 1 tend to corroborate the findings of Hume, et al⁽²⁾ with regard to vanadium. Hume's regression equation suggests that a 100 ppm increase in

vanadium would increase air reactivity by approximately 0.06%/min (0.11 to 0.17 %/min).

Experiments 2 & 3 indicate that the impact of vanadium on coke and anode air reactivity is considerably less than any previously published work researched by the authors (0.024 to 0.04%/min for a 100 ppm increase in vanadium).

Additionally, if one assumes that the sodium in the cokes tested in Hume's work was primarily internal sodium, then experiment 3 also corroborates her regression expression (a 100 ppm increase in internal sodium increase air reactivity by 0.01 to 0.03%/min).

The authors strongly feel that control of external sodium on both coke and anodes will achieve the largest reduction in air burn in commercial smelters. Minimizing sodium contact with green coke in the coke drilling, storage and handling, calcined coke upon cooling and in anode fabrication should be a primary focus in efforts to minimize air burn.

References

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