

## IMPURITY REMOVAL FROM PETROLEUM COKE

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### Abstract

The question of treating high-impurity coke to enable use in anodes was examined. A mineralogical analysis of different cokes demonstrated that more than 99 % of the particles contained the expected concentrations of sulfur, nickel, and vanadium while a small number of particles contained inclusions of other impurities. A number of potential treatment options were identified and investigated, with thermal desulfurization being studied further. The initial sulfur concentration, residence time and calcination temperature had the highest influence. 45 % sulfur removal was achieved but with significant bulk density loss. Acceptable pilot anode quality was not achievable even with the fines fraction substituted with desulfurized material. Therefore while sulfur removal during calcining is possible, the resulting coke, even in the most promising scenario, is not suitable for anode manufacturing. At this time, an industrial process to remove sulfur and other impurities from petroleum coke is unlikely to be viable.

### Introduction

As outlined in previous research [1], the quality of anode-grade coke is declining. As a recent example, the vanadium (V) and sulfur (S) levels in green coke produced in the US Gulf are presented in Figures 1 and 2, respectively.

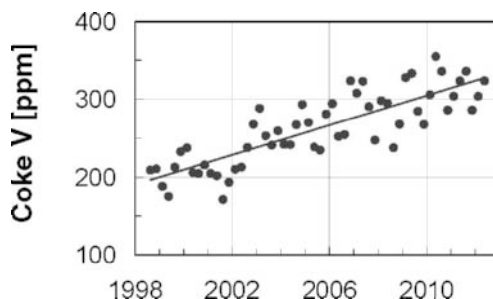


Figure 1

Concentration of vanadium in anode-grade green coke (weighted average of US Gulf Pace blends [2])

The concentration of V in anode-grade coke increased steadily over recent years reflecting the increasing V concentration in the refinery feed. The situation is somewhat different for S, the concentration of which increased steadily until 2006. Since then, the S content has not exceeded ~3.5 %. This value corresponds to the maximum S level in green coke that allows most smelters to comply with sulfur dioxide (SO<sub>2</sub>) emission limits without installing scrubbers. A reasonable interpretation of the S data is therefore that the S increase until 2006 mirrored the S increase in the refinery feed. Once a non-negotiable limit was reached, the use of high-S cokes in the blends had to be limited and/or more

low-S cokes had to be used. This resulted in higher prices for low-S cokes.

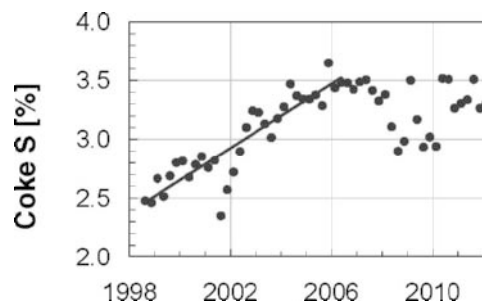


Figure 2

Concentration of sulfur in anode-grade green coke produced at the US Gulf (weighted average of Pace blends [2])

Considering the increased use of high-impurity, oil sand-derived material in refinery feedstocks, it is reasonable to assume that the anode coke quality deterioration and price increases will continue in the foreseeable future. There are several options to reduce the coke impurity concentration or to limit their negative impact. These include:

- Use of low-impurity coker feedstock materials.
- Impurity removal from coke.
- Removal of impurity-loaded secondary alumina fines.
- SO<sub>2</sub> scrubbing.

Use of low-impurity coker feedstock materials is considered uneconomical. Typically, coke represents only a small portion of the refinery revenue. This does not justify the use of more expensive, low-impurity coker feed to make more valuable low-impurity coke [3]. It is also possible to reduce the concentrations of S, Ni, and V in coker feedstock by hydrogenation [4,5]. However, the costs are usually not justified by the increased coke value.

Removal of impurity-loaded secondary alumina fines reduces the concentration of phosphorous and volatile metals in the electrolytic bath and the produced aluminum [6]. Again, this might not justify the costs of the process.

SO<sub>2</sub> scrubbing at the calciner, anode baking oven, and the smelter is technically feasible. Most of the SO<sub>2</sub> is emitted at the smelter. However, the SO<sub>2</sub> concentration in the pot room gases is relatively low [7], which translates to high scrubbing costs.

As unfavorable economics eliminates these approaches, impurity removal from coke is the remaining option, which potentially offers important advantages. Just one quarter of the green coke available is presently considered calcinable [8]. Much of the

remaining coke does not meet required purity standards. A process capable of reducing the coke impurity content would therefore considerably enlarge the anode-grade coke pool and could reduce procurement costs. This motivated Rio Tinto Alcan to revisit/explore different methods for impurity removal from coke.

### Coke Characterization

Prior to discussing various impurity removal methods, the microscopic characterization of several medium and high-impurity green and calcined cokes is presented in Table 1 and Figures 3-5.

Coke	S [%]	Metals [ppm]					Dominant texture
		Ca	Fe	Ni	Si	V	
A	3.61	70	210	210	320	490	Anisotropic
B	4.03	20	50	280	40	540	Anisotropic
B <sup>a,b</sup>	3.44	70	635	255	145	535	Anisotropic
C	5.37	80	410	230	130	500	Isotropic
C <sup>a</sup>	4.34	80	400	260	180	570	Isotropic
D <sup>b</sup>	3.80	60	220	180	83	430	Anisotropic
E <sup>b</sup>	5.50	-	-	-	-	-	Anisotropic

<sup>a</sup> Calcined

<sup>b</sup> Not studied by microscopy, used in desulfurization study

For all coke samples studied, the large majority of the particles (>99 %) had a similar appearance in the backscattered electron (BSE) images. An example for this is the particle labeled “I” in Figure 3. The relatively consistent grey level of these coke particles indicates a homogeneous distribution of the various elements. This was confirmed by the corresponding S element map (Figure 4). Here, the intensity of turquoise coloration reflects the S concentration. With the exception of the particle labeled “II”, the S concentration in the different particles was similar and uniform within them. Comparable behavior was also observed for nickel (Ni) and V (not shown). Furthermore, the concentrations of S, Ni, and V at different positions of the “type I” particles were very close to their average concentrations in the bulk sample. Apparently, these elements were evenly dispersed in the coke matrix.

A very small fraction (<1 %) of the particles displayed discrete, bright regions in the BSE images as observed in particle “II” in Figure 3. These spots indicate the presence of impurities with much higher atomic weight than carbon. The corresponding element maps for silicon (Si) and iron (Fe) showed indeed a higher concentration of these elements at some locations (dimensions <10µm). Higher local concentrations of other elements such as calcium (Ca), potassium (K), sodium (Na), titanium (Ti), and zinc (Zn) were also discovered in particle “II”. Finally, while S, Ni, and V were generally homogeneously distributed throughout particle “II”, elevated concentrations of these elements were found at some locations. However, in the element maps, the additional concentration of S could only be visualized when the contrast was enhanced (not shown), indicating only small additional quantities of S at these locations.

These results suggest that any physical separation process (for example based on differences in particle density) could not remove critical coke impurities such as S, Ni, and V. Other, less-critical, impurities (for example Fe and Si) are concentrated at

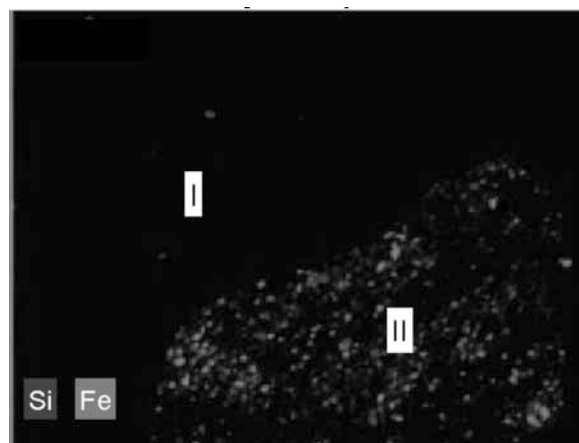


Figure 3  
Backscattered electron image of green coke A

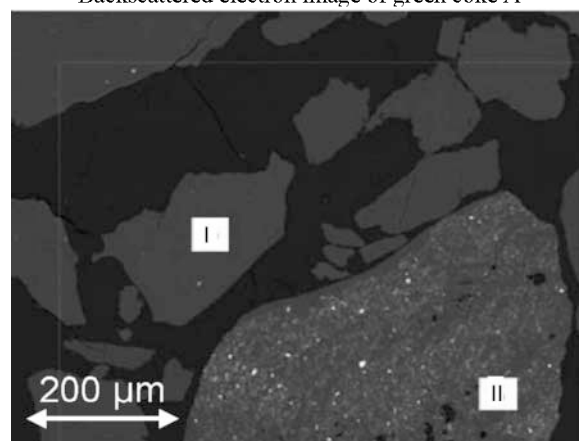


Figure 4  
Element map of S for green coke A

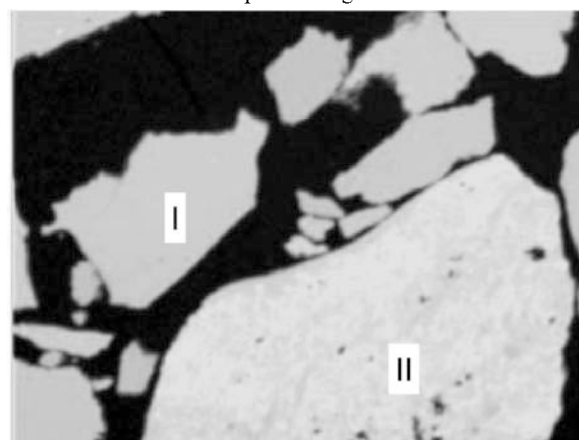


Figure 5  
Element maps of Si and Fe for green coke A

some locations of a few particles. However, any physical separation would require very aggressive particle size reduction to sizes below 10 µm in order to liberate these high-impurity portions. Based on these findings it was concluded that physical separation is not suitable to remove impurities from coke. Thus, thermal, chemical, and biological methods were studied.

## Chemical and Biological Methods for Impurity Removal from Coke

Several chemical methods for impurity removal are discussed in the literature including:

- Leaching with liquid acid and bases [9,10].
- Salt roasting [11].
- Leaching supported by microwaves [12].
- Extraction with various organic solvents [13].
- Treatment with various gases at elevated temperatures (>700°C) [9,13,14].
- Desulfurization by microorganisms [15].

Treatment with gases at elevated temperatures would require an additional dedicated high-temperature reactor. Considering the capital and operation costs, unattractive economics was assumed and these options were not further pursued. Extraction with organic solvents was also not further considered as only small reductions were reported [13].

Conversely, salt roasting is performed in other industries on a commercial scale [16] and considerable removal of V and S from coke has been reported [11]. Thus, salt roasting in combination with acid/base leaching was studied. The tests were performed under relatively mild conditions assumed to correspond to reasonable costs on commercial scale.

### Salt Roasting Tests

The general procedure for the leaching tests was as follows:

- Samples of coke B, (green and calcined, respectively) were crushed to <math>300\mu\text{m}</math> and mixed with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).
- The mixture was heated.
  - The objective of this roasting step was to transform impurities by oxidation into soluble species.
- The samples were leached with water.
- In the final step, the samples were leached with an acid or base in different tests (Table 2).

Salt roast	H <sub>2</sub> O leach	Acid/base leach	
6:1 mixture (coke:Na <sub>2</sub> CO <sub>3</sub> ) heated to 450 °C for 3 h	70 °C for 24 h	3M reactant, 70 °C for 72 h	H <sub>2</sub> SO <sub>4</sub>
			HCl
			NaOH
			Na <sub>2</sub> CO <sub>3</sub>

The crushing step would limit use of the purified coke to the fines in the anode recipe. Alternatively, an agglomeration step would be required. However, it was assumed that only fine particles provide access for the roasting/leaching agents to react with the impurities.

Acid/base leach	Impurity reduction relative to initial [%]			
	S	Ni	V	Fe
H <sub>2</sub> SO <sub>4</sub>	1	20	21	62
HCl	13	27	30	15
NaOH	12	<sup>a</sup>	21	15
Na <sub>2</sub> CO <sub>3</sub>	10	<sup>a</sup>	16	8

<sup>a</sup> Apparent enrichment during treatment

The effectiveness of the purification treatment differed for the various elements. The S content of green coke B was reduced by some 10 %, except when treated with sulfuric acid (Table 3). In this case it is possible that some sulfates remaining in the coke masked S removal. Most of the S is present as organic species, however there are also inorganic S compounds, such as sulfides and sulfates that together may account for some 20% of the total S [17]. It is possible that the treatment described here mainly removed S from these inorganic compounds.

Higher S removal rates were reported for salt roasting [11] and acid leaching (without roasting) [10] of finer coke particles than studied here. However, this would make use of the demineralized material in anodes more challenging.

Some 20 – 30 % of the Ni and V were liberated using acid treatment, while alkaline leaching media produced much poorer results, particularly in the case of Ni. These metals are present as organometallic compounds (porphyrins or metal chelates) [18]. Apparently, the treatment was able to liberate Ni and V from a portion of these compounds.

Up to 62 % of the Fe was removed by salt roasting followed by leaching with sulfuric acid. As opposed to Si, Ni, and V, Fe is mainly present as inorganic compounds and is concentrated in distinct locations of some particles (Figure 5), which appears to have facilitated removal. Similar observations were also made for other elements such as Ca (not shown).

Finally, removal of S, Ni, and V from calcined coke (Table 4) was lower as compared to the corresponding green coke (Table 3). This could be explained by several changes occurring during calcination:

- Thermal desulfurization preferentially removed S that is also removable by roasting/leaching.
- Shrinking of the coke structure limited access of the roasting/leaching reactants to impurities in the coke particle interior.
- Changes of the texture (healing of defects) made the organic coke portion, containing the impurities, less reactive.

Acid/base leach	Impurity reduction relative to initial [%]			
	S	Ni	V	Fe
H <sub>2</sub> SO <sub>4</sub>	1	4	4	87
HCl	1	4	2	79
NaOH	0	<sup>a</sup>	2	15
Na <sub>2</sub> CO <sub>3</sub>	1	<sup>a</sup>	2	30

<sup>a</sup> Apparent enrichment during treatment

The situation was different for Fe. Here, removal from the calcined coke was higher than for green coke. Apparently, the changes discussed above did not apply to the inorganic Fe compounds. It is possible that during calcination, Fe compounds reacted to products that were easier to leach (such as by decomposition of pyrite).

The following conclusions can be drawn from the tests:

- Reasonable impurity removal was only reached for elements present as predominantly inorganic species (such as Fe and Ca).
  - Concentration of these elements in coke is presently not a major concern.

- For green coke, low to moderate impurity removal was reached for the most critical impurities (S, Ni, and V).
  - Minimal removal of these elements from calcined coke was achieved.

In summary, the straightforward salt roasting and leaching approach described is not suitable to reduce the concentration of critical coke impurities to desired levels from the material tested. It is reasonable to assume that more severe conditions would have resulted in higher impurity removal. However, this would be associated with higher costs, and thus it was concluded that an industrial salt roasting/leaching for petroleum coke is unlikely to be viable.

#### Leaching supported by microwaves

Additional alkaline leaching tests were performed in the presence of microwaves (microwave frequency of 2.45 GHz and power of 640 W). Mixtures of 20 g green coke C and 150 ml of 5 N NaOH and KOH solutions, respectively, were heated to 100 °C. Afterwards, the samples were washed with water until a pH value of 7 was reached. No measurable reduction of S, Ni, and V was obtained.

#### Desulfurization by microorganisms

Tests were performed with two green coke samples (coke A and B). The microorganism culture was obtained by mixing samples from hydrocarbon-contaminated soils, waste water from a water treatment plant, and active compost. Coke samples (20g, particle size <1mm) were mixed with 200ml nutrient solution (composition as in ref. [19]) and the microorganism culture. Different agitated mixtures were kept at pH values of 4 and 7 and temperatures of 30 and 55°C, respectively, for 17weeks. The highest coke desulfurization reached was 0.8% (based on initial sulfur). Clearly, the bio-desulfurization method studied is not suitable for green coke.

#### **Thermal Methods for Sulfur Removal from Coke**

It is well-known that the S content of coke is reduced during calcination, especially when the calcination is performed under higher-than-standard temperatures [20]. High-temperature calcination might therefore be used to shift sulfur dioxide (SO<sub>2</sub>) emissions from the pot rooms to the coke calciner. This would allow the capture of a larger portion of the coke S at the calciner. As the SO<sub>2</sub> concentration in the calciner flue gas is much higher than in the pot room gases, the scrubbing costs would be lower.

However, thermal desulfurization is associated with creation of coke porosity. Anodes made with desulfurized coke therefore have undesired low bulk densities. It can be assumed that a portion of the porosity created during thermal desulfurization is lost during grinding of coarse coke particles. This might limit the negative impact of porosity creation on the anode properties. In order to verify this hypothesis it was decided to calcine a high-S coke at elevated temperatures and to manufacture laboratory anodes with the corresponding fines.

#### Pilot Calcination Runs

Pilot calcination runs were performed with three different green cokes: cokes A, C, and D (Table 1). The pilot kiln used was described in a prior publication [21]. An important advantage of this kiln is that it well replicates calcination on commercial scale. The calcination temperatures were varied between 1300 and

1500°C. These temperatures roughly correspond to the present commercial calcination temperature and to the maximum temperature that might be reached on at that scale.

The desulfurization behavior (Figure 6) and development of the calcined coke vibrated bulk density (VBD, Figure 7) observed in the present work are in agreement with work of others [20]:

- Desulfurization increases with increasing green coke S content, calcination temperature, and residence time.
- High-S cokes desulfurize at lower temperatures than low-S cokes.
- Desulfurization is accompanied by a VBD decrease.

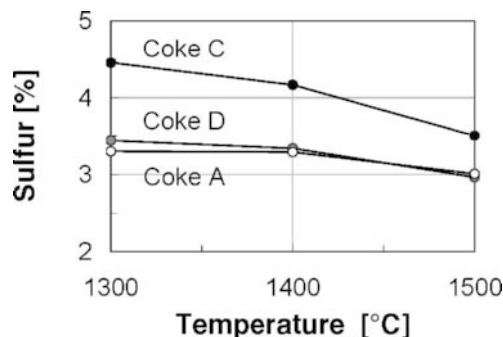


Figure 6  
Sulfur content of coke after pilot calcination at different temperatures, heating rate: 50 °C/min, residence time: 5 min.

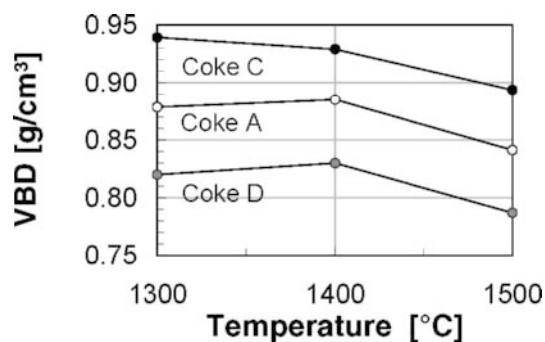


Figure 7  
Calcined coke VBD (Alcan method) after pilot calcination at different temperatures, heating rate: 50 °C/min, residence time: 5 min.

In addition to these expected results, some interesting observations were made. Due to its highly isotropic texture, coke C had a very high VBD (0.94g/cm<sup>3</sup>, after calcination at 1300 °C). Calcination at 1500 °C reduced the S content by about one third. Even higher desulfurization (~45%) was reached by increasing the residence time from 5 to 10 minutes. In spite of the associated porosity creation, the VBD was still acceptable (0.89g/cm<sup>3</sup>, residence time of 5 minutes). In fact, coke C calcined at 1500°C had a similar VBD and S content as Coke A calcined 1300°C (typical for commercial kilns). Apparently, high-temperature calcination of a high-S green coke yielded a product close to medium-S coke calcined under standard conditions. Given these promising results it was decided to manufacture laboratory anodes with coke C, partly desulfurized at 1500 °C.

Considering other impurities, the concentration of Ni and V increased during calcination at 1500°C (for example by 120 and 150ppm, respectively, for coke C, Tables 1 and 5). These non-volatile impurities are concentrated as volatile organic compounds are lost during calcination. High-temperature calcination therefore cannot be used to reduce Ni and V.

#### Laboratory Anodes with Desulfurized Coke

Laboratory anodes were made with the reference coke and coke C, calcined at 1500°C. As compared to the reference coke, coke C had a higher bulk density and impurity concentrations (Table 5). In the reference recipe, the reference coke was used in all fractions, whereas in the test recipe the fines fraction (<0.3 mm, Table 6) of the reference coke were replaced with coke C. Green anodes were manufactured at five different pitch levels. Properties of the test and the reference anodes are compared at their respective optimized pitch level, indicated by maximum baked anode density (BAD).

Coke	Reference	Coke C, calcined at 1500 °C
VBD [g/cm <sup>3</sup> ]	0.83	0.89
S [%]	1.1	3.5
V [ppm]	30	650
Ni [ppm]	141	300

Fraction [mm]		Mass [%]	Recipe	
Max.	Min.		Reference	Test
13.20	9.50	9.0	Reference coke	Reference coke
9.50	4.75	15.5		
4.75	2.36	13.5		
2.36	1.18	14.0		
1.18	0.60	10.0		
0.60	0.30	9.8		
0.30	0.15	5.2	Coke C, calcined at 1500 °C	
0.15	0.075	3.4		
0.075	0.045	2.6		
0.045	0.000	17.0		

Upon the use of desulfurized coke C in the fines, the green and baked anode densities decreased significantly (-0.04g/cm<sup>3</sup>, Table 7). This appears surprising as coke C has a higher VBD than the reference coke (Table 5). However, it is known the thermal desulfurization preferentially creates microporosity [22] that is not

Property	Change*
Green anode density [g/cm <sup>3</sup> ]	-0.04
In-situ coking value [%]	+0.7
Shrinkage [%]	0.0
Baked anode density [g/cm <sup>3</sup> ]	-0.04
Electrical resistivity [μΩ·m]	+9.1
Air residue [%]	-30
Young's modulus [GPa]	-1.0
CO <sub>2</sub> residue [%]	+7.5

\* At respective optimized pitch contents

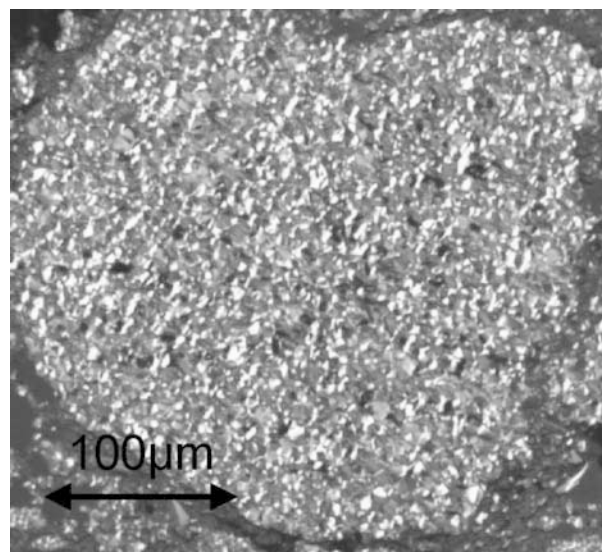


Figure 8

Micrograph of a particle of coke C, calcined at 1500 °C, in a baked anode. Porosity appearing black.

filled by pitch during paste manufacture. Thus, porosity created during desulfurization remains in the green and baked anodes. Micrographs of baked anodes showed that indeed voids in desulfurized coke particles were present (Figure 8). Other factors had a limited impact on the BAD, for example shrinkage and the in-situ pitch coking value were very similar for both anode series (Table 7).

Furthermore, use of desulfurized coke increased the electrical resistivity and decreased the Young's modulus considerably. Presently, no explanation for this observation can be given. Finally, the oxidation behavior of the anodes can be explained by the different impurity content of the cokes. As compared to the reference coke, the desulfurized coke contained much more Ni and V which favored air oxidation. However, even after partial desulfurization, the S content was still high enough to inhibit CO<sub>2</sub> oxidation.

It can be concluded that introduction of desulfurized coke in the fines fractions considerably deteriorated important anode properties, particularly the BAD.

#### Summary and Conclusions

The concentration of critical impurities (S, Ni, and V) in anode coke is expected to increase. These elements are evenly dispersed in the coke matrix, which makes physical separation techniques inapplicable. Chemical methods, performed at mild conditions as required for commercial processes, did not reduce impurities substantially enough to develop a viable process. A significant proportion of the S can be removed via high-temperature calcination. The trade-off is an important bulk density loss. Even under favorable circumstances (high bulk density coke, use of desulfurized coke in the fines), the quality of the corresponding anodes is poor. Impurity removal from cokes at the commercial scale is therefore unlikely to be viable in the near future. Thus, other techniques should be studied or revisited.

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