# The Problem of Sulfur Content in Calcined Petroleum Coke

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*The sulfur content of petroleum coke has steadily increased in recent years, and forecasts show levels will rise even further. This increase in sulfur content comes at a time when environmental awareness is at a peak, and regulatory restrictions are likely to place limits on the amount of sulfur permitted. Fortunately for aluminum smelters, several methods of reducing the sulfur content in petroleum coke appear to be viable.*

## INTRODUCTION

One of the most commonly asked questions among petroleum coke producers and consumers within the aluminum industry is, "What will happen to the sulfur content in calcined petroleum coke?" To answer this question, we studied the trend of sulfur content in petroleum coke, worldwide aluminum smelter sulfur requirements and alternatives for making reduced sulfur cokes.

Figure 1 shows green petroleum coke production in the noncommunist world between 1979 and 1988. Of the total 27 million tonnes produced in 1988, approximately 22 million tonnes were produced in the U.S. By the year 2000, we estimate that total annual petroleum coke production will be approximately 33 million tonnes.

Not all green petroleum coke is calcined. Figure 2 shows use patterns; most is burned as fuel. For aluminum anode use, approximately seven million tonnes are calcined. An additional two million tonnes are calcined for special applications, such as graphite, titanium dioxide and steel. The quality of the coke used can vary substantially.

## REFINING AND COKE PRODUCTION

For more than a century, crude oils containing high yields of gasoline and light fuels have been preferentially refined. As a result, the crude remaining in reserve today is heavier and has a higher sulfur content. In the future, refiners will process crude oil containing more sulfur and a greater concentration of heavy components.

In a modern integrated refinery (Figure 3), refining begins at the distillation unit where crude oil is separated into several fractions; these may be called light ends, medium oils and heavy oils. The "atmospheric residuum" is routed to a vacuum distillation unit for further separation. The "resid" of the vacuum distillation unit, usually 20–30% of the crude volume, is routed to the coker. There, through a high temperature destructive distillation process, more light ends and oils are produced for further processing into gasoline and light fuels. Gasoline and light fuels make up about 95% of the refinery output by volume; the value of these products is approximately 98% of the total refining revenue. Green coke, which makes up 4–6% by volume, has only 2% of the value of all the products from this refinery. As a result, refiners develop processing schemes and purchase their crudes to maximize the return on the lighter products, and minimize green coke production.

The sulfur content of green coke over the past ten years is shown in Figure 4. Sulfur increased during this time due to the increase in sulfur content of crude oil. In 1988, the average content was 3.4%. Early in the 21st century, the green coke sulfur content will approach 4%.

Figure 5 shows a dramatic increase in petroleum coke vanadium content between 1979 and 1985. The introduction of very heavy crude oil into petroleum refining led to this increase. In 1988, the average vanadium content was approximately 550 ppm; by the year 2000, it will approach 600 ppm.

## CALCINED COKE PRODUCTION AND QUALITY

The quality of calcined petroleum coke is significantly different from average green petroleum coke quality. Obviously, superior quality green cokes are selected for calcining. Table I shows the typical calcined coke quality for aluminum smelting by regions of the world. Based on these values, we estimate that the sulfur content of calcined petroleum coke supplied to the aluminum industry averaged about 2.1% in 1988.

To project calcined petroleum coke sulfur content in the year 2000, we reviewed regional crude oil refining patterns, including the types of crude oil

**Table I. 1988 Typical Calcined Coke Quality**

| | Sulfur (%) | Vanadium (ppm) |
|---|---|---|
| U.S. West Coast | 2.6 | 325 |
| U.S. Gulf Coast | 2.3 | 250 |
| Canada | 2.5 | 250 |
| Latin America | 0.8 | 100 |
| Europe | 1.2 | 85 |

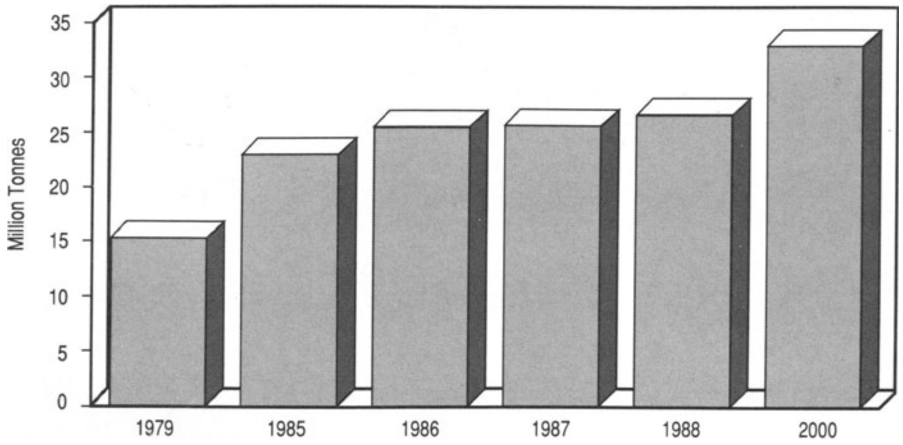


Figure 1. Petroleum coke production in the noncommunist world.

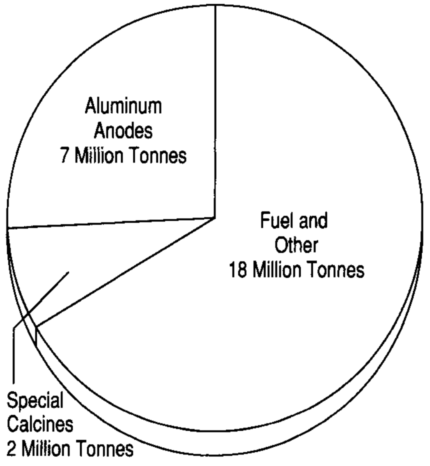


Figure 2. Green coke applications in the noncommunist world for 1988.

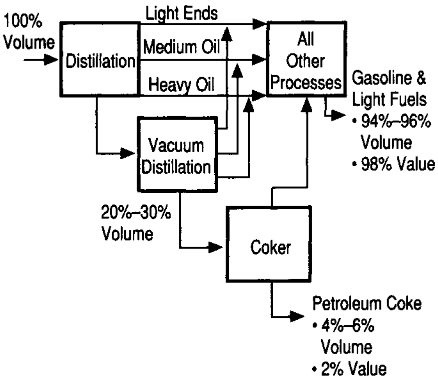


Figure 3. Diagram showing the role of coking in the petroleum processing industry.

typically processed. Petroleum coke sources in the U.S. West Coast area are refineries that process predominantly Alaskan North Slope crude oil. Since sulfur and vanadium concentrations are relatively stable for Alaskan crude oil, sulfur and vanadium increases in petroleum coke will be gradual, but small. Latin America and Europe are in similar situations with stable sources of low-sulfur crude oil. The U.S. Gulf Coast and Canada produce approximately 60% of the petroleum coke necessary to meet the needs of the world aluminum industry. Refiners supplying green petroleum coke in these regions must import much of their crude oil (the U.S. now imports over 50%). Between 1986 and 1988, sulfur levels in petroleum coke increased 12%. Further increases are certain as demand for refined products increases, requiring more and certainly heavier crude oil to be processed.

To determine the calcined coke demand, we made the assumptions listed in Table II. Based on these assumptions, demand for calcined petroleum coke by the aluminum industry in the noncommunist world will reach 6.5 million tonnes by the year 2000.

Our projections of sulfur content in green petroleum coke, coupled with the projected demand for calcined coke, indicate that the average sulfur content of calcined petroleum coke will reach 2.6% by the year 2000. This assumes that no major developments in petroleum refining or coke calcining will allow a reduction in petroleum coke sulfur. Incremental sources of calcined petroleum coke supply will likely contain more than 3% sulfur. This compares to the average calcined coke sulfur specification of 2.1% that prevailed during 1988.

## ALUMINUM SMELTER SULFUR RESTRICTIONS

Sulfur emissions from aluminum smelters are insignificant (0.2%) relative to manmade sulfur dioxide emissions from other industrial processes.[1] However, since most smelters are regulated locally, some may have to reduce the sulfur content of their raw materials to meet environmental emission standards. The smelters located near urban areas are generally under tighter regulations than those in rural areas.

In Europe and Scandinavia, a petroleum-coke sulfur limit of 2% maximum is frequently imposed locally. Many older smelters in North America are allowed to use sulfur-containing coke at the "historical" levels. For newer smelters in North America and Australia, there appears to be a 3% maximum. Latin America, South Asia and Africa generally have few restrictions on sulfur levels in calcined coke.

Due to the emphasis on acid rain in Europe and North America, it is probable that sulfur limits will tighten. But, as refiners process higher sulfur crude oil, petroleum coke supplies will contain more sulfur.

## ALTERNATIVES FOR MAKING REDUCED SULFUR COKES

With a potential crisis on the horizon for aluminum producers in the U.S. and Europe, two questions must be answered. First, what factors can affect this trend? Second, how can the coke calcining and aluminum smelting industries cope with higher sulfur coke?

A partial answer may be found in Figure 6, which shows the flow of sulfur in crude oil through the refining, calcining and smelting processes.[1] In each step, possibilities for reduction of sulfur content are shown. Since this summary was developed by Mannweiler and Frankenfeldt in 1985, we have updated the progress in each reduction step. The conclusions are discussed below and then summarized in Table III. The selection of low-sulfur crude oil as a solution is not addressed because the problem is rooted in a shortage of such oil.

### Desulfurization of Coker Feed

Figure 7 is a schematic diagram of the process for hydro-desulfurization of coker feed.[2] In this process, hydrogen, residual oils and catalyst are exposed to high temperatures and pressures. Hydrogen is added to the oil components and sulfur is removed. Such a process provides light products for further refining (which basically justifies any refiner's installation of this process). Sulfur-containing gases provide a source of elemental sulfur for sale as a product. Spent catalyst is removed and, in some cases, reprocessed. Some purified residual oils are available for coking; this depends on coking economics.[3]

In the noncommunist areas, 30 of the 618 refineries operating today have some form of residual oil hydro-desulfuriza-

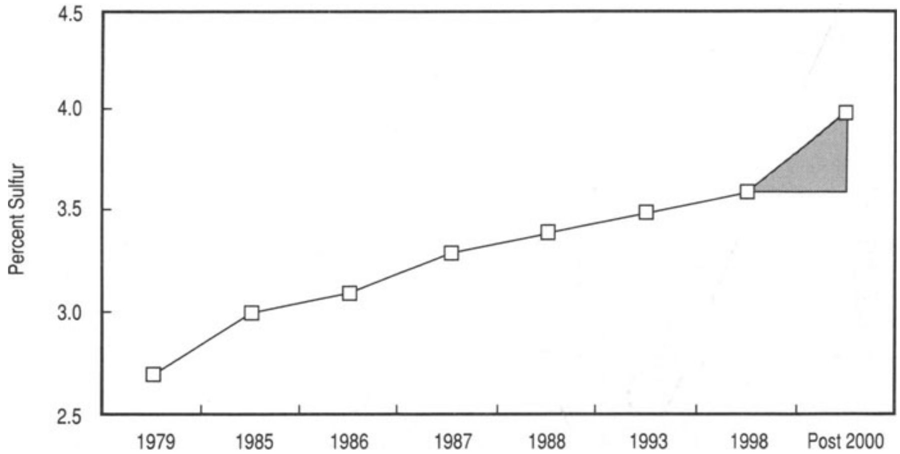


Figure 4. Sulfur content in green petroleum coke for the noncommunist world. Shaded areas indicate the range of future values.

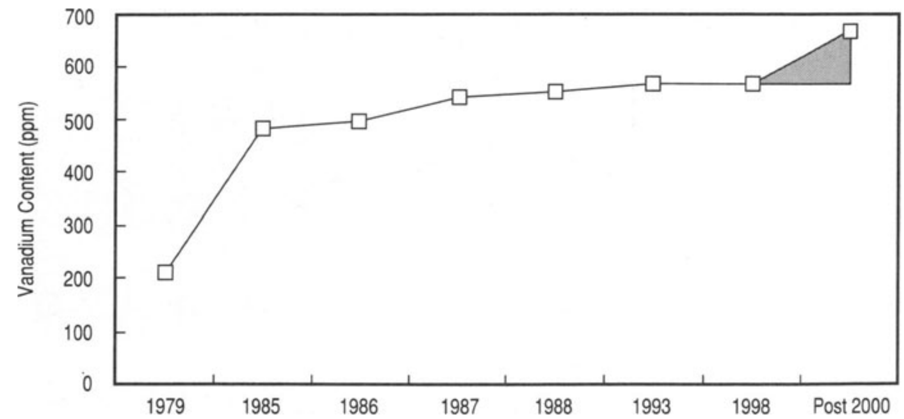


Figure 5. Vanadium content in green petroleum coke for the noncommunist world. Shaded areas indicate the range of future values.