ANALYSIS OF INDUSTRIAL COKE SAMPLES BY ACTIVATION WITH CYCLOTRON PROTONS

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Abstract.- A Melbourne Petrochemical Company was experiencing excessive coke formation in its "cracking furnaces", which was causing unnecessary stoppage of production and wastage of energy due to additional insulation. In order to investigate the possible causes of this excessive coke formation, we analyzed various coke samples and other coke-like materials obtained from these furnaces by activation with cyclotron-protons. Our results showed that, out of the two suspected coke promoters As and Sb whose small concentration in feed would produce greatly accelerated coke formation, As could not be detected in any of the eight samples investigated, while Sb was present in only one sample. However, we did observe Ca, Cr and Fe in all the samples, with surprisingly high concentrations in some of them. It has, therefore, been suggested that Ca, and perhaps Cr and Fe, but not As or Sb, could have been responsible for the excessive coke formation in the "cracking furnaces".

1. Introduction.

A Melbourne petrochemical company was in need of identifying the elements within their cracking furnaces, which were promoting the formation of unwanted coke at a higher than usual rate. The function of the cracking furnace is to break down long-chained gas oil molecules into smaller ones by introducing superheated steam at high temperatures under carefully controlled conditions. The products then undergo several processing stages to finally yield ethylene, propylene, butadiene and gasoline products. The formation of carbon is inevitable, but this has been occurring at about twice the normal rate. Decoking operations are, therefore, more frequent with subsequent loss of production. Furthermore, the coke acts as an insulator, necessitating an increase in furnace temperature to maintain the cracking reactions. This increase in temperature is not only expensive but also undesirable, since it may approach that at which the cracking tubes soften and rupture with potentially disastrous results.

The known promoters for coke formation in petrochemical plants are arsenic and antimony and, to a lesser extent perhaps calcium (private communication with K. Fuller, of the Altona Petrochemical Company, Melbourne). Even low levels of As and Sb present in the feed can produce greatly accelerated rates of coke formation. An analysis of the coke samples from the cracking furnaces should, therefore, reveal the presence of any one or both of these elements. The company concerned did not favour the use of atomic absorption method, since the analyses of both As and Sb with this technique are subject to interferences unless these elements are firstly isolated using the chemical techniques, and there is always a risk of sample contamination when wet chemical methods are used. It was, therefore, decided to use a nuclear analytical technique which did not require excessive sample handling and preparation, and thus minimized the risk of sample contamination. We chose to use activation with cyclotron protons for the analysis of As, Sb and Ca in coke samples, which appeared to be well suited for these elements.

Moreover, this also fitted nicely into our extensive experimental and theoretical programme on charged particle activation using cyclotrons.[1] Besides determining the levels of As, Sb and Ca in various samples, it was thought that perhaps some other elements could also be investigated which, on their own or in combination with Ca, As or Sb, could play important roles in this process of coke formation.

2. Method.

Eight different coke and coke-like samples were provided by the Company for analysis. Some of the samples were in powdered form, while others were partially crushed. In all cases the samples were crushed to a fine powder, using an ultra-clean grinder-cum-stirrer, which also ensured homogeneity. A "standard" was prepared by doping one of the samples with 1170 ppm Ca, 790 ppm Ti, 460 ppm Cr, 2380 ppm Fe, 3600 ppm As and 1400 ppm Sb. The samples for irradiation were prepared by compressing the powdered coal into recessed grooves of an aluminium target holder, and covered with a thin layer of aluminum foil. The aluminum foil was held down in position with aluminum brackets.

The target holder was placed in an insulated scattering chamber, and the whole target chamber assembly acted as a Faraday cup for monitoring the beam current/charge on the samples. Each sample was irradiated with 8.5 MeV protons for 1 hour at a current of 1 μA, using the Melbourne University Cyclotron. During each run the target assembly was cooled with liquid nitrogen in order to avoid any target deterioration during irradiation. The volume of liquid nitrogen contained in the target arm was sufficient to last for more than an hour.

The irradiated samples were allowed to wait for an hour before being counted with a Ge(Li) detector and a PDP-Computer Analysis System. This waiting period of one hour was necessary in order to reduce the high induced short-lived activities, which caused immense pile-up problem in the counting system. The gamma ray spectra from the activated coal samples were analyzed using the computer programme SEARCH, developed in our laboratory.[2]

This programme searches various gamma peaks, assigns them to the corresponding elements, subtracts the background for individual peaks and integrates the peak areas along with the respective errors.

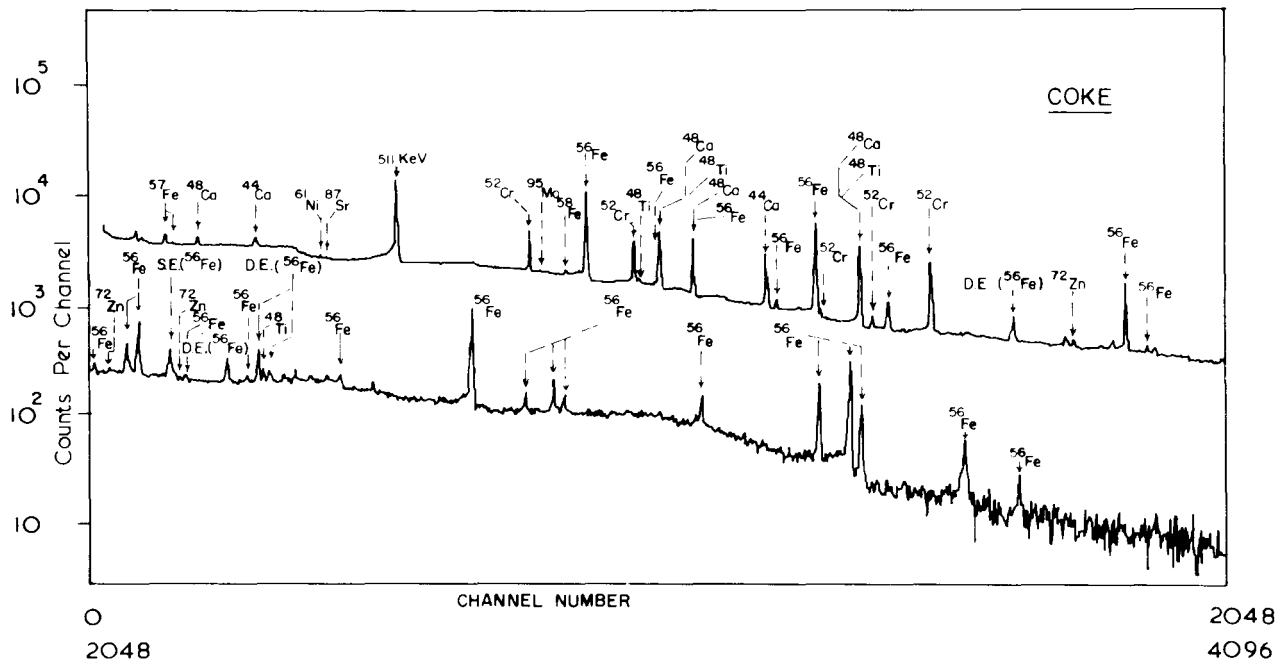3. Results and discussion.-

Fig. 1. A Ge(Li) gamma spectrum from an activated coal sample

A typical gamma spectra from one of the activated coal samples is shown in Fig. 1. All the peaks in the spectrum have been identified with the computer, [2] and have been accordingly labelled. The elements assigned to different peaks are those which, after activation with 8.5 MeV protons, would give rise to these gamma ray peaks. From the areas underneath these peaks, and by comparison with the corresponding peak areas of the "standard" sample, the concentrations of various elements present in the samples were calculated. The results are summarized in Table 1.

Table 1 - Results of proton activation analysis on coke samples

Element	Standard (dopant added)	Sample Number							
		1	2	3	4	5	6	7	8
Ca	1170	6	20	830	4400	75	165	48	15
Fe	2380	500	430	13000	39000	725	36500	2110	880
Ti	790	<6	<6	480	1200	<14	<120	<22	<13
Cr	460	98	8	2650	1250	<4.6	5170	350	80
As	3600	<7	<7	<7	<7	<3.4	<30	<6.6	<4.0
Sb	1400	<30	<30	<30	<30	68	<36	<11.5	<5.4

Concentrations are in ppm by mass. Errors are typically < 10%

The coke samples are listed in the table by number only, since details such as their exact ages (after decoking), as well as their positions inside the furnaces, were not available.

It can be seen from the table that Ca, Cr and Fe were present in all the samples; Sb was found in only one of them; while As could not be detected in any of the samples with the sensitivity of detection available with this technique. However, it was possible to estimate the upper limits for presence of As and Sb in all the samples.

Similarly, Ti was found in only two of the eight samples, while for the remaining six the upper limits for Ti were calculated.

The results summarized in the table indicate that, contrary to the general belief, no evidence could be found for the presence of As and Sb in the coke samples and, therefore, these elements could not be held responsible for excessive coke formation in the cracking furnaces. It seems likely that Ca, which was observed in all the samples, and in relatively high concentrations in at least two samples, was involved in this coking phenomena. Similarly, the possible involvement of Cr and Fe cannot be ruled out.

It is quite possible that As and Sb could have still been present in the samples and involved in the coke formation, but at concentrations which were beyond the limits of detection by the present technique. Similarly, there could have been other elements too, which were present in the sample but could not be detected by activation with 8.5 MeV protons. However, in spite of such possible shortcomings, our method did point out the possible relevance of Ca, Cr and Fe in the excessive coke formation, which in itself is quite useful information.

In conclusion it can be said that activation analysis, using 8.5 MeV protons from a cyclotron, has proved to be a simple and useful technique for elemental analysis of coke samples with minimum detection limits of only some parts per million in most cases. With this technique it has been shown that Ca, and perhaps Cr and Fe, are responsible for excessive coke formation in the cracking furnaces, and not As and Sb, which were suspected to be the main culprits.

References:

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