Trace Elements in South African Coal – Evaluation of Trace Element Distribution in the no. 4 Seam, Witbank Coalfield

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ABSTRACT

South Africa remains the 5th largest producer and joint 4th largest exporter of coal in the world. It is also a major supplier of coal to the European Union. This is significant as the European Union has recently supported the environmental lobby that threatens the combined full scale use of coal in Europe and other first world countries. This promotes the development of clean coal technologies in order to counter the ever increasing number of environmental constraints threatening the export market. One critical development in clean coal technologies is coal beneficiation, which allows the reduction of mineral content. Permian coals from South Africa have characteristically high ash and inertinite contents and therefore require further beneficiation. The no. 4 Seam in the Witbank Coalfield is no exception, and it can be described as containing higher inertinite content and minerals compared to the no. 2 Seam in the same Coalfield. Beneficiation, therefore, is an important requirement for improving the quality of the coal, especially for export purposes.

With the increase in environmental legislation and the drive towards “clean coal” a concern is raised in terms of the performance and marketability of export coal produced from the no. 4 Seam in the Witbank Coalfield. This seam is economically significant and remains an important source of export steam coal.

This paper reports on the investigation of the trace elements, within the seam, its distribution and association with the organic and inorganic components of the coal. Float and sink fractions obtained from densimetric separation were analysed for trace elements using ICP-MS. The relationship between coal mineralogy, petrography and trace element distribution, methods of optimum trace element reduction is established. Furthermore, the distribution of mineralogical and organic components of sulphur in the no. 4 Seam is shown to bear unique relationships with certain trace elements. By assessing the distribution and occurrence of trace element concentrations in density fractions (obtain by float and sink tests as well as by froth flotation), data was produced which can be used to better evaluate and promote products obtained from the beneficiation of the no.4 Seam coal.

Keywords: Trace Elements, Permian Coals, Witbank Coalfield, Marketing, Washability, Mineralogy

INTRODUCTION

According to the latest report by the Department of Minerals and Energy (Prevost, 2004) the Highveld and Witbank coalfields account for approximately 66% of the remaining coal reserves in South Africa. Historically, the no. 2 Seam in the Witbank Coalfield was the main target for exploitation, but its reserves have declined significantly over the last 2 decades, leading to the no. 4 Seam becoming increasingly the main source of export products. The no. 4 Seam in situ coal is known to be higher in ash and inertinite, or “dirty” as described by Lurie (2000), when compared, for example, with the no. 2 Seam. Therefore, beneficiation of the 4 seam is imperative and its upgrade to yield an export grade product has been successfully achieved over the years, through incremental improvements in techniques and equipment. The export product is mainly used as solid fuel for pulverised fuel combustion in utility boilers. With the advent of new and improved technologies and expanding opportunities for exporting to foreign markets, and with requirements from recent environmental legislation, the availability of trace element washability and floatability data could play a major role in promoting the utilization of coal products from no.4 Seam in the Witbank Coalfield.

The risk associated with trace element emissions lies both in health risks and in financial cost implications when seeking to remain within legislative measures. Certain trace elements such as HAP (Hazardous Air Pollutants) can have substantial implications, and according to James and Hower (2004) the US Clean Air Act Amendments of 1990 specifically identified As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se, and U as potential HAP’s. These trace elements are known to be toxic and have adverse effects on humans, plants and animals as identified by Dale (2003).

There is limited data available on the matter of trace elements in South African coals The trace elements Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo are concentrated in the mineral matter in the coal (Ruch et al., 1998). For this reason, beneficiation by density separation should be able to assist in reducing not only the mineral content of a coal, but also the trace elements associated with such minerals. Legislative measures in most developed countries are increasingly strict and South African coal exporting companies are interested in contributing to finding solutions to reducing or eliminating dangerous emissions. Cairncross et al (1990) has reported that the mercury content in South African coals is, for instance, higher than the global average, but subsequent work by Ruch et al (1998) and Wenfeng et al (2006) it seems as if coal beneficiation can reduce the mercury content significantly by the removal of the related minerals.

Most significant in the study of trace elements, is the association of these elements with either the epigenetic or syngenetic minerals. The latter form is typically finely disseminated in the coal matrix, therefore extremely difficult to fully separate from its organic substrate. Given that Gondwana coals particularly those in South Africa, India and Brazil characteristically contain high quantities of inherent minerals and near gravity material, coal producers often find themselves constrained in attempting to achieve the desired product through conventional beneficiation. In contrast, epigenetic or extraneous minerals are successfully liberated from the coal matrix by a relatively straightforward separation process.

It is the objective of this investigation to contribute to better understanding of South African coals, and thus to promote the industrial utilisation of South African coals from the Witbank Coalfield.

Witbank Coalfield 4 Seam background

Concentrations of trace elements often vary within the coal seam and are associated with the sedimentary deposition. The Carboniferous coal measures in the northern hemisphere (Laurasian) are known to be overlain by strata of marine origin, and therefore tend to have higher sulphur and generally higher trace element contents when compared with those associated with non-marine sediments mostly typical in South Africa (Wagner and Hlatshwayo, 2004). The geology of the seam is important in assessing the associated sulphur and the trace element distribution. Cairncross et al (1990) reported that sedimentological investigations of the coal-bearing Vryheid Formation (Karoo Sequence) in the Witbank Coalfield have revealed that coal-peat deposition was associated with both marine and non-marine depositional events.

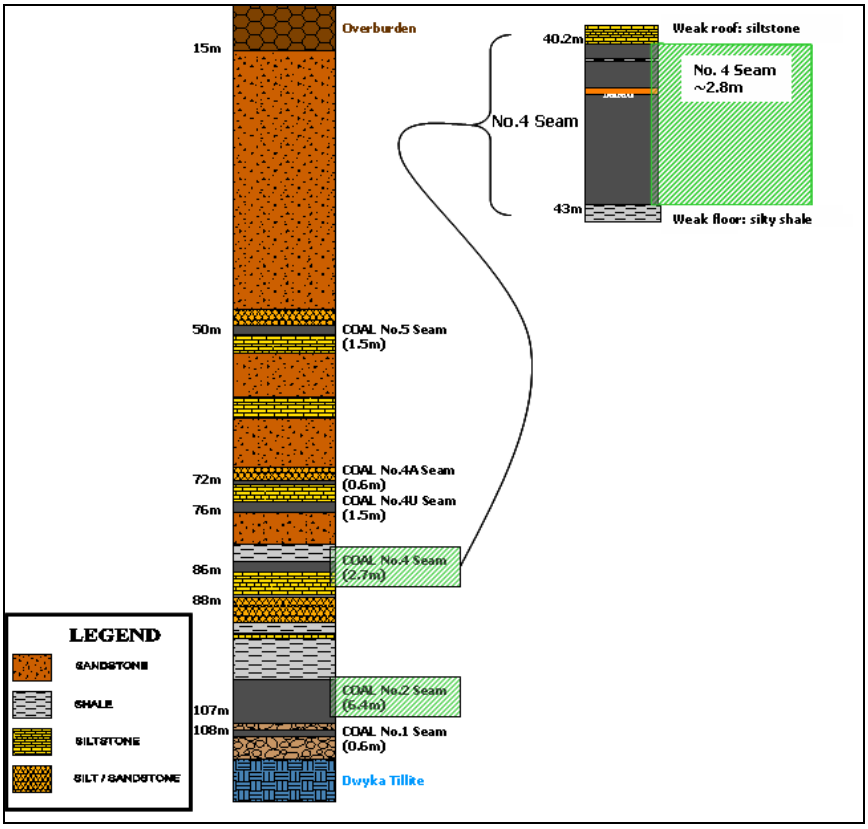

Figure 1: Stratigraphy of the no.4 Seam, Witbank Coalfield (*Courtesy of Anglo Coal Mine Geology Department*)

At the mine where the samples were taken the particular section of the no. 4 Seam ranges in thickness from 2.2 to 3.3 m, averaging 2.8 m (Figure 1). This seam may split and resulting in the upper 4 and upper 4A seams above the 4 Seam itself. However, these splits are not of economical importance and therefore not mined. In such instance an in-seam limonitic mudstone parting of up to 0.2 m in thickness typically separates a lower better quality zone of mainly dull lustrous coal with an average thickness of 1.9 m from an upper poorer quality zone of mixed dull and bright coal averaging 0.7 m.

EXPERIMENTAL PROCEDURES

Sampling

A series of no. 4 Seam run of mine (ROM) coal were collected. These samples were taken over a period of 24 hours with the aid of an automated mechanic sampler. The samples were taken in accordance to the SANS ISO 13909-2 Standard.

Slurry samples of flotation plant feed; product and tailings were also collected by means of mechanical samplers. These samples were taken in accordance to SABS ISO 20904. The flotation plant feed slurry samples were used to do bench scale froth flotation tests.

Sample preparation

The ROM samples were suitably prepared by homogenizing several times prior to any reduction in mass or in nominal top size, then cone and- quartered to produce a single set of samples for washability analysis. The samples were transported to Anglo Coal Central Laboratories (ACCL) within 2 hours where the remaining of sample preparation and analyses took place. When stored, the samples were kept in a controlled environment indoors.

Float and Sink Washability analysis

Float and sink densimetric separation was carried out with the use of Zinc Chloride (ZnCl) as dense medium (ISO 7936:1992). The total sample was floated and the fine fraction was not removed prior to the washability analysis. Each resulting density fraction and the sink were suitably prepared for all planned laboratory analyses. Proximate analysis and calorific value analysis was done on each density fraction.

Flotability analysis

For the bench scale tests a conventional Denver froth flotation cell was used. A combination of 200 g of 4 Seam flotation plant feed ultra-fines at minus 200 µm and 3L of water were preconditioned without air and reagent. The reagents used in the test work were a combination of 80% collector (mainly kerosene) and 20% frother (glycol and emulsifiers), 0.3mℓ reagent was dosed into the slurry and further conditioning time of 30 s was allowed. Upon the addition of air, a further 2.5 min was allowed for flotation with scraping done every 20 s. Proximate and calorific value analyses was carried on each of the flotation fractions feed, tailings and product.

Trace element analysis

Trace element analysis, total sulphur (organic, pyritic and sulphate) was outsourced to UIS analytical. Trace element analysis was done by UIS analytical services and consisted of microwave digestion followed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

In the microwave digestion test a mixture of nitric acid, hydrochloric acid and hydrofluoric acid were used. The samples were heated to approximately 210°C at 20 atm. After a first stage of digestion a second one was performed to ensure that all the material was dissolved. Stock solutions were used for the determination of a variety of trace elements in the digests by ICP-MS.

Mineral and liberation analysis

The XRD (X-Ray Diffraction) analysis was outsourced to the University of Pretoria mainly for the identification and quantification of mineral species. The method of Quantitive Evaluation of Materials by Scanning Electron Microscopy (QEM SEM) or QEMSCAN was employed at ESKOM Research & Development for the identification and the determination of the mass percentage, liberation characteristics and distribution of mineral species.

RESULTS

Given the sensitive nature of the data generated by this project, locations of the samples are identified only as a no .4 Seam samples one and two.

Composite sample results

Concentrations of several trace elements were obtained, but only a few of them were evaluated to date. In Table 2 the concentrations of trace elements in the feed (or ROM) and beneficiated fractions are reported, and compared with results of other seams obtained from literature.

When compared to the global average published by Zhang et al (2004), most of the trace element concentrations in the ROM are higher affirming the need for further beneficiation of the feed. The lower density fractions show much lower concentrations when compared to the feed and sinks fraction (+1.80 RD). It is therefore clear that removing minerals by density separation reduces the trace element concentration. The observation is made that washing at low densities (below 1.40 RD) does not necessarily constitute a low trace element concentration in the product in all cases.

Trace element association

The main method used in evaluating and deducing the mode of occurrence of the trace elements in this project is washability characteristics. This can be done, but only with a concurrent evaluation of the mineral species and their liberation. Heavy minerals in particular, may not be sufficiently liberated and might occur in the finely distributed form in the low density float fraction. This was found to be the case not only for pyrite, but also for the radioactive element bearing minerals. The other indirect method employed for deducing the mode of occurrence of a trace element was by evaluating other coal quality parameters, for instance the relationship between certain trace elements with the sulphur species. However, this approach was undertaken cautiously as it could be potentially misleading, and a thorough mineralogical evaluation is required to verify the relationships.

Consequently statistical correlation and mineralogical investigation were used to determine the highest degree of association. Minerals identified in the no.4 Seam and associated trace elements are given in Table 1.

Table 1: Trace elements and associated minerals for Witbank Coalfield no. 4 seam

Mineral	Associated element
Pyrite	As, Cd, Co, Cu, Hg, Mo, Ni, Pb, Se
Apatite	F,Cl
Clays (kaolinite and illite)	Cr, Mn, V

The majority of the trace elements proved to be associated with the pyrite in the coal. The pyrite associated trace elements are typically of major concern.

Trace elements associated with pyrite

From the results in Table 1 and the mineralogical investigations, the association of the trace elements to the mineral species is established. In Figure 2, it is evident that arsenic follows closely trend of the pyrite. Statistically the data between the per cent pyrite and arsenic concentration indicates a correlation of 98 per cent.

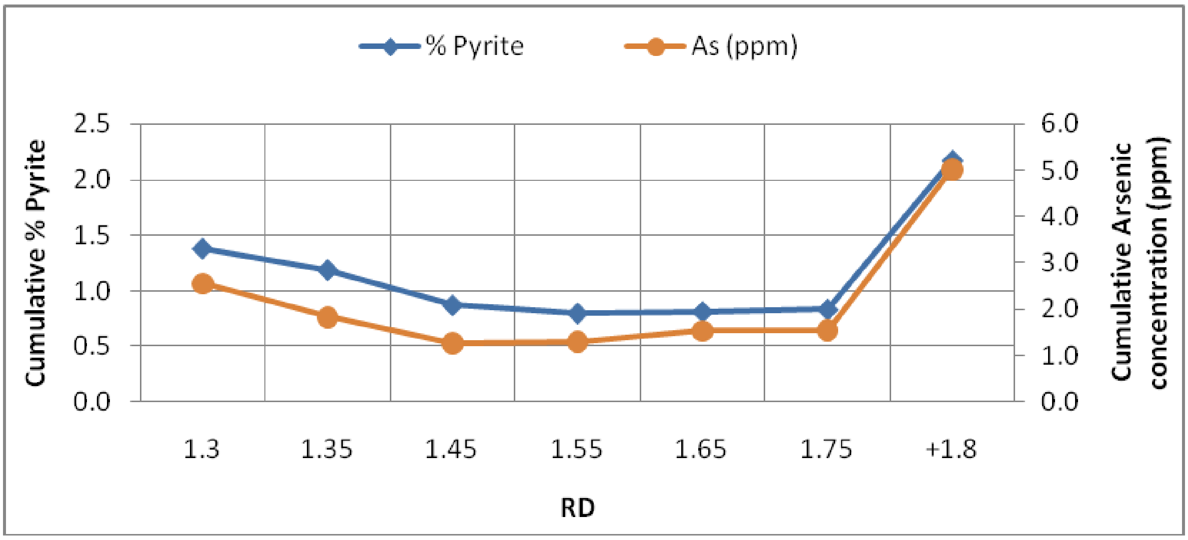

Figure 2: The relationship between pyrite (by XRD) and arsenic concentration at various densities

The relationship in figure 2 is similar to the other trace elements associated with the pyrite content in the coal, namely As, Hg, Mo, Pb, Se, Mo, Cu, Ni and Cd.

However, the case of arsenic and mercury is more complex, since two forms of arsenic and mercury species occur. Arsenic for example occurs as pyritic and organic arsenic in the coal. The increased arsenic concentration in the lower density fractions can be attributed to poor liberation of the pyrite particles and also to the organic arsenic associated with the organic sulphur in the high vitrinite fractions.

Table 2: A summary of historical and current results for feed (composite) and washed samples

		Range Global Swaine, (1990)	Global Zhang et al., (2004)	Witbank Coalfield 2 Seam Cairncross et al., (1990)	Highveld Coalfield 4 Seam Wagner and Hlatshwayo (2004)	Average Product Float Concentrations Witbank Coalfield 4 Seam							
						Feed	1.30	1.40	1.50	1.60	1.70	1.80	Sinks (+1.80RD)
Ash	%					25.0	4.5	7.8	11.7	14.0	15.8	16.9	28.2
Major													
Arsenic	mg/kg	0.5–80	5	4.6	3.14	4.7	3.8	3.4	2.2	2.0	2.0	2.0	18.8
Cadmium	mg/kg	0.1–3	0.6		0.44	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.36
Lead	mg/kg	2–80	25	10	7.51	15.03	13.09	9.83	9.51	9.55	10.07	10.39	29.3
Mercury	mg/kg	0.02–1	0.12		0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.76
Molybdenum	mg/kg	0.1–10	5		1.18	2.1	3.3	2.1	1.5	1.4	1.3	1.3	6.78
Selenium	mg/kg	0.2–10	3	0.9	1.05	1.2	0.9	0.6	0.8	0.6	0.6	0.7	1.39
Moderate													
Chromium	mg/kg	0.5–60	10	28	70.5	41.4	38.7	31.2	31.2	29.6	29.5	29.7	112
Copper	mg/kg	0.5–50	15	9.7	13.2	16.8	17.6	20.3	17.3	16.6	15.9	15.8	25.3
Nickel	mg/kg	0.5–50	15	17	21.1	27.2	34.7	28.2	23.1	21.1	20.4	20.1	70.3
Vanadium	mg/kg	2–100	25	27	33.5	39.2	68.7	50.9	37.2	33.9	32.9	33.0	58.6
Minor													
Antimony	mg/kg	0.05–10	3	0.47	0.32	0.5	0.7	0.7	0.3	0.3	0.3	0.3	0.87
Cobalt	mg/kg	0.5–30	5	7.9	6.3	11.0	24.9	24.9	14.0	11.4	10.5	10.1	14.6
Manganese	mg/kg	5–300	50		19.6	163.	35.2	50.6	70.2	75.9	83.4	89.7	151.9
Radio Active													
Uranium	mg/kg	0.02–5.5	3.1	4.0		2.6	4.0	3.0	2.5	2.4	2.4	2.4	3.61
Thorium	mg/kg	0.1–12.2	1.9	15.0		8.9	5.4	9.9	11.2	9.9	9.4	9.2	8.15

Reduction of trace elements

The reduction potential of the trace elements by beneficiation was established by calculating the percentage reduction in concentration. The formula used in the calculation is given by equation 1.

$$\%\,\mathrm{Reduction} = \frac{x_{\mathrm{Feed}} - x_{\mathrm{Product}}}{x_{\mathrm{Feed}}} \times 100\% \qquad \text{[Equation 1]}$$

Where x_n = Cumulative Trace Element Concentration (ppm) and n = Feed & Product

Reduction by dense medium beneficiation

The manner in which the different trace elements behaved with beneficiation varied. We considered dense medium beneficiation at densities between RD 1.30 and 1.75, and evaluated the percentage reduction obtained for each element. In Table 3 the results show that the percent reduction (calculated with Equation 1) of the trace elements varies with different densities. A negative reduction indicates an increase in trace element concentration when compared with the concentration in the feed.

Table 3: Percentage reduction obtained with dense medium beneficiation at different cut-point densities

	Percentage reduction at different cut-point densities					
Component	1.30	1.35	1.45	1.55	1.65	1.75
Ash	82%	64%	48%	38%	29%	24%
Major concern						
Arsenic	14%	17%	51%	67%	78%	82%
Cadmium	*-18%*	28%	17%	23%	22%	20%
Lead	12%	32%	34%	35%	35%	33%
Mercury	13%	34%	30%	38%	40%	40%
Molybdenum	*-69%*	2%	7%	19%	26%	27%
Selenium	14%	17%	51%	67%	78%	82%
Moderate concern						
Chromium	*-29%*	3%	4%	11%	13%	13%
Copper	*-29%*	*-31%*	*-15%*	*-3%*	3%	4%
Nickel	*-76%*	*-27%*	*-1%*	10%	15%	16%
Vanadium	*-81%*	*-42%*	0%	10%	14%	14%
Zinc	27%	40%	34%	31%	31%	26%
Minor concern						
Antimony	*-68%*	*-2%*	39%	39%	41%	41%
Cobalt	*-95%*	*-94%*	*-28%*	*-3%*	7%	10%
Manganese	97%	84%	70%	67%	66%	65%

Reduction by *froth flotation*

The degree of reduction of the trace elements investigated with froth flotation was lower compared to that observed in dense medium beneficiation. A lower reduction is obtained for trace elements associated with pyrite. The froth flotation of pyrite occurs readily with the coal because of its surface characteristics. This is identified as the main reason for lower degrees of reduction with the pyrite associated trace elements (As, Hg, Mo, Pb, Se, Mo, Cu, Ni and Cd).

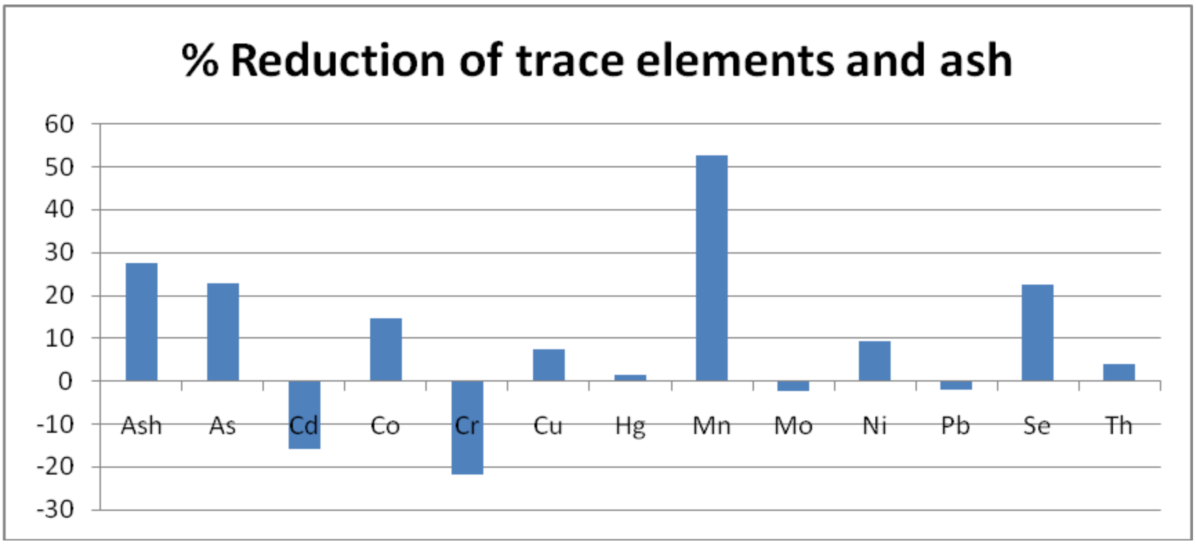

Figure 3: Witbank Coalfield no. 4 Seam – Reduction in trace elements by froth flotation

In contrast to the pyrite associated trace elements, flotation proved to be highly effective in the removal of manganese, see Figure 4. Manganese is typically associated with carbonate minerals, and in some instances with clays. From the washability results obtained, manganese follows the kaolinite content in the coal.

In summary, the concentration levels of trace elements in beneficiated fractions indicates that they are mainly associated with minerals, and can be removed by density separation so as to reduce the potential effects to the environment, when such coals are consumed in power generation plants. A multi-stage wash at different operating densities would allow improved beneficiation. The modelling of maximum reduction or the reduction capacity factor will permit matching specific coals for prospective markets. The specific product trace element and sulphur content can be modelled to evaluate the possibility of being utilised in advanced gasification processes and in the production of synthetic organic chemicals.

CONCLUSIONS

- There exists a relationship between the trace elements and both the organic (maceral) and inorganic (mineral) components in the no. 4 Seam coal.

- The concentrations of most trace elements in the final marketable coal product can be manipulated by beneficiation. However, a low operating density to obtain as low as possible ash in the coal product does not necessarily constitute a product with a low specific trace element concentration.

- The volatile trace elements of concern which have a higher concentration than the global average in the ROM coal include mercury, arsenic and molybdenum, whilst those that occur in proportions lower than the global average include selenium, cadmium and lead. A multi-stage wash is recommended as a possible beneficiation technique to remove mercury and arsenic.

- Arsenic and mercury are not only associated with the mineral pyrite, but are also linked to the organic sulphur components in the coal. The organic sulphur in the no. 4 Seam has been proven to be related to the vitrinite maceral in the coal.

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