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Short communication

Relationships between noble metals as potential coal combustion products and conventional coal properties

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ABSTRACT

Increasing coal consumption has generated million tons of ash and caused various environmental issues. Exploring statistical relationships between concentrations of valuable metals in coal and other coal properties may have several benefits for their commercial extraction as byproducts. This investigation studied relationships between conventional coal concentrations and concentration of noble metals for a wide range (708 samples) of eastern Kentucky coal samples (EKCS) by statistical methods. The results indicate that there are significant positive Pearson correlations (r) $>$ 0.90 among all noble metals (Au, Pt, Pd, Ru and Rh) except for Ag (r $<$ 0.2). The results also showed that the noble metals (except Ag) are associated with the minerals of the coal and have high positive correlations with ash (and high negative correlations with the organic fraction). Modeling through the database demonstrated that the highest Au concentrations in the EKCS occur when Si is between 6000 and 8000 ppm and Fe is below 10000 ppm, and the highest Ag was observed when both Cu and Ni were over 40 ppm. Outcomes suggested that aluminosilicate minerals and pyrite are possibly the main host of noble metals (except Ag) in the EKCS whereas Ag might occur in various forms including organic association, mineral species, and as a native metal.

1. Introduction

Since electricity usage has grown, coal consumption has continuously increased in electric power plants [1–3]. As a result of this progress, one of the critical problems for traditional thermal power plants is generation of millions of tons of ash [4]. It has been estimated that combustion of four tons of coal potentially can produce one ton of coal ash. Dumping of this substantial volume of coal ash can be a source of various environmental problems (such as water and soil pollution) and waste a considerable amount of valuable elements (gold, silver, rare earth elements (REEs), titanium, aluminum, scandium, gallium, vanadium, etc.) [5–7]. Thus, companies have started to develop various technologies to recover these valuable elements from coal combustion products. The first commercial extraction of metals from metalliferous coals was reported in USA in the 1800s [8,9]. As a result of increasing coal consumption, several investigations have recently been conducted into the extraction of valuable metals from coal [10–14].

Currently, industrial scale activities for extraction of gold, silver, aluminum and germanium from coal combustion products and ash have been developed in different countries; however, most approaches are still in the initial stages of industrialization and further investigations are required to turn them into reality [4,5]. Grzymek [15] established specific methods to recover alumina from coal fly ash and two plants with capability of producing hundred thousand tons of alumina per year have been constructed in Poland [16]. The extraction of germanium from coal fly ash by a two-step leaching process, with rejection of impurities and then foam recovery of Ga at 95% recovery was developed by Fang and Gesser [17]. The extensive occurrence of noble metals (i.e. Au, Ag, and PGE) in coal has attracted attention for their economical extractions [18]. The first recovery of Au- Ag from coal was developed in Wyoming and South Dakota (USA) more than 100 years ago [8,9,18]. Gold was recovered from wastes of the Reftinsk power plant in Russia [19], and Vysotsky [20] proposed the potential extraction of platinum group (PEG) from coal. Ketris and Yudovich [21] reported the average of gold content of world coals is around 3.7 ppb. In general, coal containing around 50 ppb noble metals potentially can be considered as an ore [18]. A combination of pre-desilication of fly ash and sintering by lime-soda was suggested for extraction of noble metals (simultaneous extraction of noble metals as a group was recommended) [22].

Generally, the value of the noble metals depends upon their concentrations in the coal which is significantly related to the coal's source

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and diagenetic history. On the other hand, an accurate valuation of noble metals is quite complicated, involving full-scale tests and generation of representative samples. Limitations in analytical techniques may also be critical since many compounds of noble metals are volatile at a relatively low temperature (300–400 °C) [4,18]. Therefore, exploring relationships between concentration of noble metals and conventional coal properties may have several advantages where the decision-making for processing developments and extraction of valuable metals from coals (as byproducts) is based on the data which can show relationships between those elements and the minerals or organic compounds within the coal structure [23]. Furthermore, such a study may help to better understand the mechanisms of formation for noble metals in coal samples [18,24]. Although some investigations have studied the mechanisms of accumulation of noble metals in coal [5,18,19], understanding the relationships between noble metals and coal properties (proximate, ultimate, ash oxides, and other trace elements) for a wide range of samples is still not well understood. The main aim of this investigation is to assess correlations between noble metal concentrations and a range of conventional analytical properties for a range of eastern Kentucky coal samples (EKCS) (708 samples) using statistical methods.

2. Materials and methods

A realistic evaluation of relationships between various elements in the coal and conventional properties requires a robust database to cover a wide variation of coal characteristics. Statistical assessment of such a database can generate outputs with a high degree of validity. In this study, the data used to assess the relationships was obtained by U.S. Geological Survey (USGS) from eastern Kentucky [25]. Coal samples with high volatile bituminous rank were selected to avoid possible variations which may occur in lower or higher rank materials. A total of 708 analyses were considered which included proximate and ultimate analysis, major element oxides and trace elements on a “whole-coal basis”. Since noble metals are volatile at a relatively low temperature, any analytical technique which includes high-temperature treatment of samples can be inadequately efficient [18]. Therefore, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to record trace elements within the coal samples. The conventional analyses were conducted based on the standard ASTM test methods. The descriptive statistics of the conventional coal analysis results and the noble metal concentrations (Au, Ag, Pt, Pd, Os, Ru and Rh) are given in Table 1. To explore the relationships between various coal properties, Pearson correlation (r) was performed through the database. The correlation coefficient “r” was used determine statistical correlations between pairs of continuous parameters. The r value provides information about the magnitude of the association, and the direction of correlations. The “r” value can range from −1 to +1, where +1 represents a perfect positive correlation, −1 shows a perfect negative association, and 0 means no statistical correlation exists. Statistically, “r” values above absolute 0.6 means a strong correlation exists between the relevant two variables [2,3,26]. Stepwise multivariable regression was applied to model the relationship between the noble metals and the major trace elements. In the stepwise regression modeling, all candidate inputs for the model are examined to see if their significance has been reduced below the specified tolerance level. The “first step” will identify the “best” one-variable model (with largest absolute inter-correlation with the dependent variable). Subsequent steps will identify the “best” two-variable (if it satisfies the criterion for entry), three-variable, etc [3,27]. Contour plot was used for the modeling of noble metals based on two most effective major trace elements which were selected by stepwise regression. Contour models are useful for investigating conditions which the highest or lowest concentration of a target may occur (in the present study the highest concentration of the noble metals).

Table 1
Descriptive statistics of the eastern Kentucky coal samples (whole coal basis).

Variables	Minimum	Maximum	Mean	Std. Deviation
Moisture (%)	0.90	15.90	3.54	1.92
Volatile matter (%)	25.80	48.50	36.20	3.13
Ash (%)	0.90	31.80	9.48	5.27
Hydrogen (%)	3.80	6.00	5.26	0.33
Carbon (%)	51.40	82.33	71.50	5.46
Nitrogen (%)	0.90	2.41	1.55	0.21
Total Sulfur (%)	0.40	8.90	1.67	1.29
Sulfate sulfur (%)	0.00	0.47	0.04	0.06
Pyritic sulfur (%)	0.00	7.62	0.89	1.10
Organic sulfur (%)	0.08	2.45	0.73	0.31
SiO_2 (%)	9.8	84.0	44.58	11.32
Al_2O_3 (%)	5.5	39.0	25.88	6.69
CaO (%)	0.30	22.00	1.91	1.76
MgO (%)	0.22	4.30	0.82	0.37
MnO (%)	0.00	0.94	0.02	0.06
Na_2O (%)	0.03	1.90	0.38	0.27
K_2O (%)	0.18	5.70	2.01	0.92
Fe_2O_3 (%)	0.65	88.00	17.00	15.88
TiO_2 (%)	0.01	3.50	1.32	0.54
P_2O_5 (%)	0.00	4.20	0.32	0.46
SO_3 (%)	0.00	21.00	2.19	2.13
Au (ppm)	0.05	3.40	0.67	0.41
Ag (ppm)	0.00	0.69	0.06	0.05
Ru (ppm)	0.01	1.10	0.16	0.11
Rh (ppm)	0.01	0.51	0.15	0.08
Pd (ppm)	0.01	0.52	0.07	0.05
Pt (ppm)	0.022	2.30	0.30	0.21

Table 2
Pearson correlations between noble metals in eastern Kentucky coal samples.

Noble metals	Au	Ag	Hg	Ir	Rh	Ru	Pd	Pt
Au	1.000	0.16	0.15	0.23	0.93	0.91	0.95	0.97
Ag	0.16	1.000	0.22	0.04	0.21	0.17	0.19	0.12
Rh	0.93	0.21	0.18	0.22	1.000	0.85	0.86	0.81
Ru	0.91	0.17	0.13	0.21	0.85	1.000	0.93	0.89
Pd	0.95	0.19	0.12	0.22	0.864	0.93	1.000	0.95
Pt	0.97	0.12	0.11	0.22	0.81	0.89	0.95	1.000

3. Results and discussion

Exploring the relationships between noble metal concentrations (Table 2) indicated that there are quite strong positive inter correlations ($r > 0.90$) between Au, Pt, Pd, Ru, and Rh but that there is not show a strong relationship (only a weak positive correlation) of those elements with Ag ($r < 0.2$). It has been suggested that significant correlations of Au in coal can be considered as potential indicator for presence of other noble metals [28]. These results of present study have demonstrated that inter correlations between one member of the noble metals group and other coal properties can represent similar correlations for other members except for Ag. Moreover, it has been suggested that the Ag distribution may be different from the distribution of other noble metals [18]. Thus, Au and Ag have been selected to explore relationships between noble metals and conventional coal properties.

Pearson correlations between Au and Ag and proximate analysis parameters (Table 3) showed that Au has the highest positive inter correlation with ash (r: 0.92) among the proximate parameters. Furthermore, there is a high negative correlation between Au and the parameters representing the organic part of coal (carbon and hydrogen) (Table 3) ($r \sim -0.8$). In general, four modes of occurrences have been reported for gold in coal: association with sulfides, dispersion as native Au, adsorption on clay minerals, or bonded with organics [18]. In some studies, a negative correlation between Au concentration and coal ash was reported (Au associated with the organic matter) [28], and in some a strong positive correlation with ash [18]. However, the outcomes of the present study have illustrated that in the eastern Kentucky coal