Full Length Article

# Modes of occurrence of non-mineral inorganic elements in lignites from the Mile Basin, Yunnan Province, China

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ABSTRACT

Non-mineral inorganic elements (NMIE; e.g., Al, Mg, Ca, and Fe) in lower-rank coals are released in a more reactive atomic form than the same elements in crystalline mineral particles during coal combustion and gasification, thus allowing them to participate more easily in slagging and fouling processes. Quantitative analysis of these non-mineral inorganics is therefore helpful to better understand their behavior during coal utilization. Lignite samples collected from the Mile Basin in southeast Yunnan Province, China, were studied to provide further insights into the modes of occurrence of the NMIE Al, Mg, Ca, and Fe. Geochemical and mineralogical investigations were performed using a multiple analytical approach, including a three-step sequential leaching process, oxygen plasma low-temperature ashing, X-ray powder diffraction (XRD), field emission-scanning electron microscopy in conjunction with energy-dispersive X-ray spectrometry (FE-SEM), and inductively coupled plasma mass spectrometry (ICP-MS). The Mile lignites have an elevated content of authigenic gypsum, which was deposited from dissolved $SO_4^{2-}$ and organic-bound or dissolved Ca. A large proportion of the Ca, Mg, and Fe in the Mile lignite occurs as dissolved salts, ionic species attached to carboxylates, and metallic species held in organometallic complexes, which were completely leached by water, ammonium acetate, and $NH_4$-EDTA, respectively. In contrast, only a low proportion of Al in the lignite occurs in non-mineral inorganic form. Non-mineral Fe, Al, and Ca largely occur as organometallic complexes; only a small proportion of Ca occurs in a water-soluble form or in extractable carboxylates if present. Magnesium, however, occurs in various non-mineral inorganic forms, and could be leached not only by $NH_4$-EDTA but also by water and ammonium acetate solutions. Iron is effectively leached only by $NH_4$-EDTA and the leaching does not appear to affect the occurrence of pyrite in the coals.

## 1. Introduction

Coal is a complex combustible rock made-up of an organic component and mineral matter [1]. The mineral matter in coal embraces the total inorganic constituents [2,3], including discrete crystalline mineral particles and poorly crystalline mineraloids, as well as any non-mineral inorganic elements (NMIE) that may be dissolved in the coal's pore water or associated in some way with the organic matter [2,3]. The mode of occurrence of the mineral matter is influenced in part by the coal rank. Generally, most of the mineral matter in higher-rank coals is represented by crystalline mineral particles. These may occur in lower-rank coals as well, but non-mineral inorganics may also make-up a considerable fraction of the mineral matter in lignites and sub-

bituminous materials [2–6]. NMIE have been observed to occur in lower-rank coals in many deposits around the world, such as the Bowen [7], Collie [8], Telford [9], Callide, Surat [8], and Gippsland Basins [10] of Australia; the Greymouth [11] and Huntly [8] Coalfields in New Zealand; the South Kalimantan and Bukit Assam Coalfields in Indonesia [8,12]; the Mae Moh Basin in Thailand [13]; the Ptolemais and Achlada Basins, northern Greece [14,15]; the Shengli Coalfield in Inner Mongolia, China [16], and many others. In addition to their adverse effects during coal combustion, such as abrasion, stickiness, deposit formation or corrosion in boilers [2,3,17,18] that are at least partly caused by NMIE, non-mineral inorganics (e.g., Al, Mg, Ca, Fe, and Ti) are readily released in a more reactive atomic form than that of crystalline mineral particles, thus allowing them to participate more easily in slagging and

fouling processes [19].

Studies of lower-rank coals have been conducted by a number of authors [5,6,20–24] using various methods to help to understand the modes of NMIE occurrence. For example, selective leaching techniques have been used for this purpose on some Australian and American lower-rank coals by Durie [4], Kiss and King [5], Ward [9], and Grigore and Sakurovs [10]. In-situ direct analysis, e.g., electron probe microanalysis (EPMA), SEM-EDS, synchrotron X-ray fluorescence (SXRF), X-ray absorption fine structure (XAFS), and X-ray absorption near edge structure (XANES) have also allowed non-mineral inorganics to be identified in a number of low-rank coals [7,8,25–27]. Li et al. [8], in particular, have evaluated the changes in concentration of the NMIE in coals of different rank levels using EPMA techniques.

X-ray diffraction (XRD) analysis combined with oxygen plasma low-temperature ashing (LTA) is a conventional approach for investigation of mineral matter in both high and low-rank coals [2,3]. Most of the non-mineral inorganics in lower-rank coals form the corresponding sulfates (e.g. bassanite, anhydrite, and hexahydrite) during the plasma-ashing process, and indeed these may be the dominant phases in the LTA residues [2,16,28]. These artifact minerals contribute to the dilution of the pre-existing phases (such as quartz, clay minerals, pyrite, and carbonate minerals), with the consequence that minor amounts of some mineral phases may not be detected in an X-ray diffraction analysis.

Sequential selective leaching (SSL) is an indirect method used to indicate the likely mode of occurrence of elements in coal, based on the presumption that specific elemental forms respond differently to the individual reagents used in the different leaching stages. The SSL technique has also been used to indicate possible modes of occurrence of non-mineral inorganics in lower-rank coals [6,9,10,13,23,24]. Analysis of element concentrations in the leachate can be used to evaluate the deportment of the NMIE. For example, three leaching reagents viz. water, ammonium acetate, and hydrochloric acid have been used by several authors to extract water soluble constituents, exchangeable ions, and acid soluble complexes, respectively, from low-rank coal samples [9,10]. However, in addition to leaching carboxylic-acid associated inorganics, ammonium acetate has also been reported to attack some carbonates [29,30], although Grigore and Sakurovs [10] did not find such effects on calcite in low-rank coals. In such cases, the proportions of non-mineral inorganics would probably be overestimated because of the addition of cations derived from carbonate decomposition if ammonium acetate was used in the leaching process.

In order to identify the modes of occurrence and quantify the abundance of the non-mineral inorganics in lower-rank coals, carbonate-free lignites of Early Miocene age (mean maximum huminite reflectance 0.40%), located in the Mile Basin in southeastern Yunnan Province, China, were investigated using the modified sequential selective leaching procedure outlined by Grigore and Sakurovs [10]. Diammonium ethylenediaminetetraacetate ($NH_4$-EDTA) buffered by $NH_4OH$ to pH = 9 [31,32], rather than hydrochloric acid, was used for the purpose of removing the organic-associated inorganics without effecting the mineral phases pre-existing in the coal [10]. The study has also attempted to evaluate the mineralogical compositions in the LTAs obtained from un-leached and leached coals, to better understand the mineral variations after the three-step leaching process and their relations with the modes of NMIE occurrence.

## 2. Samples studied and analytical methods

### 2.1. Sample collection

The Mile Basin is located in southeastern Yunnan Province, China (Fig. 1). The coal-bearing sequence in this basin is the Miocene Xiaolongtan Formation. The M1 Coal, with an average thickness of 35 m, is located in the lowermost section of the Xiaolongtan Formation. A total of 61 bench samples were collected from a section of the M1 Coal in the

coalfield, among which eight coal samples (Table 1) with relatively high concentrations of major elements (e.g. Ca, Mg, and Fe; as described below) were chosen for the selective sequential leaching process. Each coal bench was sampled over a channel with 10-cm width and 10-cm depth. The sample numbers and their individual thicknesses are shown in Table 1.

### 2.2. Analytical methods

Proximate analysis, including the determination of moisture, ash yield and volatile matter, was based on ASTM Standards D3173-11 [33], D3174-11 [34] and D3175-11 [35], respectively. The total sulfur was analyzed for all the samples following ASTM Standards D3177-02 [36]. Forms of sulfur were determined for samples with total sulfur higher than 1% based on ASTM Standard D2492-02 [37]. Coals containing less than 1% sulfur were not performed on the analysis of forms of sulfur as it is generally considered that sulfur in such coals is usually dominated by organic sulfur [38]. Polished grain mounts for microscopic analysis were made of the coarse-crushed coals (particle size < 1 mm) following ASTM standard D2797/D2797M-11a [39]. The mineral composition of the samples was determined by X-ray diffraction using a Rigaku D/max-2500/PC XRD diffractometer with Ni-filtered Cu-Kα radiation and a scintillation detector at the China University of Mining & Technology, Beijing (CUMTB). Prior to XRD analysis, the coals and leaching residues were processed by an EMITECH K1050X oxygen-plasma asher to remove the organic matter at a temperature of < 120 °C. In addition, the raw coals (without low-temperature ashing) were subjected to the XRD analysis. The XRD patterns of the investigated samples were processed to quantify the mineral composition using Siroquant, commercial interpretation software developed by Taylor [40] based on the Rietveld refinement approach [41]. A field emission-scanning electron microscope (FE-SEM, FEI Quanta™ 650 FEG) in conjunction with an energy-dispersive X-ray spectrometer (EDAX; Genesis Apex 4) at CUMTB was used to investigate the morphology and chemical composition of minerals in polished grain mounts made-up of raw coal particles. The major oxides in the pressed powders made-up of coal high-temperature ash (HTA, 815 °C), including $SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, $CaO$, $MgO$, $MnO$, $Na_2O$, $K_2O$, and $P_2O_5$, were determined by X-ray fluorescence (XRF) spectrometry (ARL ADVANT′XP+) at CUMTB. The percentages of major-element oxides were reported on an ash basis.

For the SSL process, ultra-pure water (18.2 MΩ.cm, prepared by a Milli-Q™ A10 system Millipore), 1 M ammonium acetate, and 0.1 M $NH_4$-EDTA buffered by $NH_4OH$ to a pH of 9 were used as the leaching reagents. It was expected that water-soluble and carboxylic-acid associated inorganic elements would be leached by the ultra-pure (Milli-Q) water and by the ammonium acetate, respectively. The elements held in chelate complexes or associated with functional groups (referred to herein as organometallic complexes) other than carboxylic groups in the coal were expected to be leached by the $NH_4$-EDTA at pH = 9, which has a negligible effect on the crystalline minerals thought to occur in the samples [31,32] and does not contaminate the extracted solutions with introduced metal cations [10]. A study by Grigore and Sakurovs [10] also confirmed that the high-pH $NH_4$-EDTA does not have any effect of on the crystalline mineral matter in coal samples. The three reagents used in this study were thus expected to effectively leach the non-mineral inorganics in the coals, without the effects on crystalline minerals that would be associated with strong acids.

Approximately 4–6 g of each powdered coal sample (less than 200 mesh) was loaded into a glass beaker. Ultra-pure (Milli-Q) water (100 mL) was added, and the suspension thoroughly stirred then left to stand for 24 h. A small amount of alcohol was added before the Milli-Q water to improve the wettability of the coal particles. The suspension was filtered using a fiberglass filter with a vacuum pump to obtain the corresponding residues. The filtrates were then stored for later analysis of elemental concentrations; the residues were transferred into 200-ml