Elution of Ti during Solvent Extraction of Coal and the Transformation of Eluted Ti upon Combustion

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Solvent extraction of coal is an effective method for removing coal ash, thereby generating the ultraclean fuel that can be directly combusted in gas turbine. Due to their organic affinity, a few inorganic elements can be extracted as well. Ti in coal extract, its elution from raw coal as well as the transformation of eluted Ti during coal extract combustion, have been investigated. Two coals of the U.S. and their acid-washed samples were extracted under 1 MPa N_2 (cold) at 360°C. The solvents used include nonpolar 1-methynaphthalene and its mixtures with polar indole. The results indicate that, Ti in coal extracts is mainly composed of nanoparticles including TiO_2 (anatase) and Ti associated with quartz. These particles are insoluble in any acids, having a fine dispersion into coal matrix. Upon coal fragmentation at 360°C, they could be librated, and, hence, traversed the filter for isolating coal extracts. The organo-Ti was preferentially extracted as well, which is most likely in a form of Ti porphyrin or Ti chelated with phenol-oxygen. These findings also have implications for revealing the modes of occurrence of Ti in the raw coals. Combustion of coal extract at 1,000°C resulted in the formation of nanometric TiO_2 polymorphs and much complex compound like $FeZnTiO_4$. The former species could be mainly formed by the phase change of TiO_2 (anatase) at high-temperatures, while formation of the latter one could involve the capture of metallic vapors like Zn on TiO_2 polymorphs. The resultant nanoparticles may escape the conventional pollution control devices, causing environmental concern. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1646–1655, 2008

Keywords: coal solvent extraction, organo-Ti, nanometer-sized TiO_2 and Ti associated with quartz

Introduction

Solvent extraction of coal is a cost-effective strategy for removing coal ash. Under the mild conditions of 200∼400°C and 1∼5 MPa, the resultant extract has a very low-ash

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content, typically of the order of 0.1wt% or less.[1–5] Such an ultraclean fuel is expected to have a variety of applications. Its direct combustion in gas turbine can achieve a power generation efficiency of ∼48%, and, hence, mitigating CO_2 emission.[6] Its hydrogenation is potential to yield more hexane-soluble light oils than that from the raw coal.[7] In addition, the ultraclean coal extract can be used as a source of high-purity carbon for carbon steel alloys.

Although coal extract has very low-ash content, the inorganic metals within it still pose a number of serious problems when such a fuel is used. For a gas turbine fuel, its inherent metals are limited to less than 200 mg/kg in total.[6] The mineral particles must be extremely finely dispersed as well.[8] Otherwise, the turbine blade erosion, corrosion and fouling can occur. For hydrogenation of coal extract, the catalyst can be deactivated by the deposition of Ti on its surface.[9–11] Recent studies have been extensively conducted on the elution of most the elements and their properties in coal extract.[12–16] Information for Ti is, however, scarce.

Ti is typically present in coals at the 300∼1,000 mg/kg (0.03∼0.1 wt%) level, having a variety of chemical forms including TiO_2 either as anatase, rutile, or as brookite, Ti associated with illite or quartz, and Ti associated with coal organic matrix (i.e., organo-Ti).[11,17,18] TiO_2 in several U.S. coals was found as discrete elongated grains <10 μm, which was mainly of anatase that was presumably formed at low-temperatures during coalification. Ti in illite or quartz is likely as finely dispersed TiO_2, or in an isomorphously substituted form. Regarding the organo-Ti, it has not been identified unambiguously in coal. It probably dominates in a low-density float fraction of coal during density gradient separations.[11,19,20] The most likely formula as found in the float fraction of Kentucky #9 coal include $(NH_4)_2TiO(C_2H_4)\cdot H_2O$, or organo-Ti (Tyzor) compounds or alkoxide compounds. In all these types, Ti is present as Ti^{4+} in distorted octahedral coordination by oxygen. A significant fraction of Ti in some subbituminous coals was suggested as chelate complexes involving phenolic hydroxyl ligands.[10] The final confirmation on these species is still lacking, because it is very difficult to isolate organo-Ti as outlined by a report relating to the isolation of gallium porphyrin.[21]

Coal extraction is commonly conducted by dissolving coal in an organic solvent at 350∼400°C in ∼1 MPa (cold) nitrogen.[1–5] Subsequently, the resulting extractable fraction is isolated by filtration using a stainless filter having a pore size of ∼0.5 μm in a laboratory-scale process. Due to their highly organic affinity, the organometals including the transition metals (Fe, Cu, Cr, Mn, Ni, Cr, etc.), and B and Hg, as well as ion-exchangeable ions like Ca and Mg, are preferentially extracted.[12–16] Such a case should apply to the organo-Ti as well. Nevertheless, the probability for elution of Ti mineral species cannot be ruled out. Given a portion of the inherent Ti-bearing particles smaller than 0.5 μm, it is reasonable for them to traverse the aforementioned stainless filter. Little is known about the quantities of individual Ti-bearing species eluted into coal extract.

The primary objective of this study is to reveal the Ti elution during solvent extraction of two U.S. coals having the different coal rank. Variation of Ti elution amount with coal extraction yield was initially investigated by employing the solvents having different polarity to extract the coals. Such an investigation can also provide information on the distribution of extractable Ti in the raw coal organic matrix. More importantly, to elucidate the chemical forms of the eluted Ti, the coals were treated by acid leaching, and the resulting coal samples were extracted as well. Acetic acid was adopted to remove the ion-exchangeable ions that are abundant in low-rank coals.[22] Sulfuric acid (7% in methanol, v/v) was used to remove the metalloporphyrins in coal.[23] By comparing the results from raw coals and acid-washed coals, we aim at distinguishing the elution of ion-exchangeable Ti and Ti porphyrin. The sulfuric acid-insoluble Ti in coal extract was identified by high-resolution transmission electron microscope (TEM).

Another objective of this study is to reveal the crystalline morphologies of Ti-bearing particles generated from coal extract combustion. Such information is useful for management on the risks relating to the turbine blade abrasion/erosion, as well as the emission of airborne fly ash when a coal extract is directly combusted in gas turbine. For this purpose, coal extract was burnt at 1,000°C. The resulting ash was observed by TEM. Mechanisms for the formation of Ti-bearing particles were discussed as well.

Experimental

Coal property

Two Argonne premium coal samples (APCS) were tested,[24] including Illinois No. 6 (IL) bituminous coal and Wyodak-anderson (WY) subbituminous coal. Both coal samples were pulverized to less than 125 μm, vacuum-dried and stored prior to use. On the mass basis of dried coal, IL coal has 40.1% volatile matter (VM), 44.4% fixed carbon (FC) and 15.5% ash, compared to 44.7% VM and 46.5% FC, and 8.8% ash in WY coal. Regarding the ash composition, Si, Al, Ca and Fe are the major elements in IL coal ash, accounting for >90 wt% on the mass basis of the total ash. They are mostly present as discrete mineral particles like clay, calcite, pyrite and illite.[16,22] On the other hand, WY coal is rich in ion-exchangeable cations (Na, K, Ca, Mg, etc.) and other organically bound species, due to its low-rank characteristic.

Coal extraction procedure

Coal extraction was conducted in a batch-scale device as depicted elsewhere.[25] As briefly explained in Figure 1, coal was initially stirred with an organic solvent under the conditions of temperature at 360°C, atmosphere at 1 MPa N_2 (cold), and time at 1h. The solvents used include nonpolar 1-methynaphthalene (1-MN) and mixed ones consisting of 1-MN and polar indole (IN). The IN percentage was 20% or 40%. Subsequently, the resulting slurry was quickly filtered at the extraction temperature. A stainless filter having a pore size of ∼0.5 μm was employed. The resulting filtrate was added with an excess of hexane (∼400 mL), and ultrasonicated for ∼20 min to precipitate coal extract. It was eventually filtered by a PTFE membrane filter having a pore size of ∼0.8 μm. The resultant precipitate, namely coal extract, was further vacuum-dried for 12 h at 80°C. Regarding the residual solvent, it contains a few amount of the light oils/tars extracted from coal that accounts for <5 wt%. No further

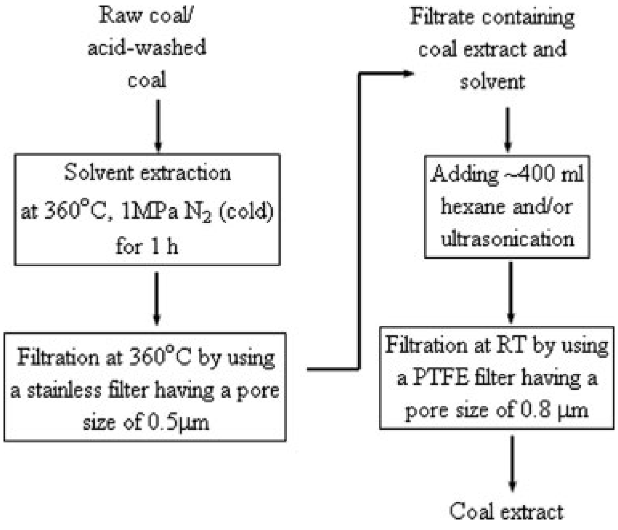

Figure 1. Laboratory-scale coal extraction process.

attempt was made to isolate the light oils/tars. Nevertheless, an elemental measurement of the residual solvent did not find any metals including Ti within it. It, thus, has little effect on the behaviors of metals during coal extraction.

Apart from raw coals, the acid-washed coal samples were also extracted. Acid washing was conducted by stirring the mixture of a raw coal (~5 g), and an acid (~150 mL) under ambient conditions for 24–48 h. Acetic acid (1 M, ultrapure grade) and sulfuric acid (7% in methanol, v/v, reagent-grade) were adopted. Such a pretreatment can improve coal extraction yield, because the cation-bridging crosslinks in coals can be cleaved.[26] Additionally, as noted earlier, by comparing the elution of Ti from both raw coal and acid-washed coal, it is desirable for us to elucidate its modes of occurrence.[14]

Coal extract combustion

Combustion of IL coal extract was carried out in a muffle furnace. The furnace was first heated to 1,000°C. Approximately 200 mg IL coal extract, having near-monolayer dispersion on a ceramic boat, was then put inside and held for ~3 min until its complete combustion. Air of ~30 mL/min was charged continuously into the furnace. After combustion, the boat was quickly moved out, and cooled in a vacuum dessicator in 20 min. Note that the ceramic boat was carefully washed before its use. It was immersed into 1 M HNO_3 overnight, rinsed with milli-Q water, and then dried in a clean bench providing a Class 100 working environment. Its contamination is negligible.

Quantification of Ti by ICP-OES

Concentrations of Ti in all samples were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). A solid sample of about 0.1 g was initially dissolved into 5 mL HNO_3 (60%, ultrapure grade), and 1 mL H_2O_2 (30%, ultrapure grade) on a microwave digestion system (Multiwave 3000, Anton Paar). The digestion conditions are: temperature, 190–210°C; holding time at the peak temperature for 90 min; pressure up to 6 MPa. After digestion, the resultant solution was filtered by a PTFE filter having a pore size of 0.45 μm (Sterile Millex-HV Millipore), and further diluted with 1 M HNO_3. The dilution factor (DF), referring to a mass ratio of final solution to a solid sample, was about 10,000 for raw coals and 150 for coal extracts, respectively.

ICP-OES analysis was performed on Optima 4300DV, Perkin Elmer. Ti was analyzed at the wavelength of 334.940 nm. A standard coal sample, NIST SRM1632c having a certified Ti concentration of 517 ± 32 mg/kg was primarily digested and analyzed under the aforementioned conditions. As presented in Table 1, Ti was measured as 519 mg/kg in this study, having a relative standard deviation (RSD) of 7.2%. In addition, measurement on the blank 1 M HNO_3 solution indicates the great sensitivity of Ti quantification, having the limit of detection (LOD) and limit of quantification (LOQ) of 0.7 and 2.3 mg/kg, respectively. All suggest the high reliability and preciseness of the selected digestion and analysis conditions. In addition, blank experiments were conducted by treating 1-MN alone and its mixture with 40% IN in the same manner to coal extraction. Ti was found lower than the LOD, suggestive of few contaminants from either the reagents or the extraction procedures used here.

TEM observations on Ti in coal extract and fly ash

TEM observation on Ti in coal extract was conducted on a JEOL JEM2100F microscope operating at 200 kV, and equipped with a high-resolution UHR pole piece and energy-dispersive X-ray spectroscopy (EDS). For sample preparation, the method as suggested elsewhere[27] was adopted. A little amount of coal extract was initially embedded into epoxy resin. After solidification, the resin was sliced by a microtoming method with a diamond knife. The resulting slice, having a thickness of about 20 nm, was transferred onto a Cu-grid for observation.

TEM observation on Ti in the combustion-derived fly ash was performed on Topcon EM-002B at an accelerating voltage of 200 kV. For sample preparation, the fly ash was initially immersed into acetone by ultrasonication. Subsequently, several droplets were directly transferred on Cu-grid for observation. Electron diffraction patterns of the crystalline phases were recorded in SAED (selected area electron diffraction) mode. The *d* spacings were compared to the international center for diffraction data (ICDD) inorganic compound powder diffraction file (PDF) database to identify the crystalline phases.

Table 1. ICP-OES Analysis of Ti in a Standard Coal Reference, NIST SRM1632c

Wavelength (nm)	334.940
Certified value (mg/kg)	517 (±32)
Found in this study (mg/kg)	519
RSD (%)	7.2
Limit of detection (LOD)* (mg/kg)	0.7
Limit of quantification (LOQ)* (mg/kg)	2.3

*LOD and LOQ were defined as the concentrations corresponding to 3 and 10 times the standard deviation of signal for a blank solution (1 M HNO_3), respectively.

Table 2. Coal Extraction Yields, wt%, daf

	Raw Coal	Acetic Acid-Washed Coal	Sulfuric Acid-Washed Coal
IL coal			
1-MN alone	54.3	52.9	40.6
1-MN mixed with 20% IN	70.3	—	—
1-MN mixed with 40% IN	68.9	74.5	85.6
WY coal			
1-MN alone	27.3	32.7	35.0
1-MN mixed with 20% IN	31.5	48.4	—
1-MN mixed with 40% IN	34.2	63.8	70.4

Results and Discussion

Coal extraction yields

Coal extraction yields are listed in Table 2. The bituminous IL coal was easily extracted relative to its counterpart. For the raw coals, about 54.3 wt% of IL coal (on the dried-and-ash-free basis), and 27.3 wt% of WY coal were extracted by 1-MN alone. Adding IN into 1-MN improved coal extraction yields. Around 68.9% of IL coal and 34.2% of WY coal were extracted when 40% IN was mixed with 1-MN.

A prior acid washing improved coal extraction yield, especially in the case of using the mixed solvents. For instance, when 40% IN was added into 1-MN, the sulfuric acid-washed IL coal and WY coal gave an extraction yield of 85.6% and 70.4%, respectively. Here again, such an effect can be explained by the cleavage of cation-bridging cross-links in coal macrostructure. The resulting small-sized fragments were readily extracted by a polar solvent.

Ti elution into IL coal extracts

As can be seen in Table 3, Ti is 886 mg/kg in the raw IL coal. It is, however, as low as 46 mg/kg in the extract generated by 1-MN alone extraction of the raw coal. With the percentage of polar IN in 1-MN increasing, Ti concentrations in coal extracts were increased obviously, reaching 117 mg/kg, and then 228 mg/kg (see column 2). Regarding the effect of acid washings, employing acetic acid gave rise to appreciable improvement on Ti concentrations. Conversely, a prior sulfuric acid washing reduced the Ti concentrations.

Table 3. Concentrations of Ti in Raw IL Coal and Coal Extracts, mg/kg

	Raw Coal	Acetic Acid-Washed Coal	Sulfuric Acid-Washed Coal
Before extraction*	886		
Extracted by 1-MN alone	46 (22)	67 (31)	18 (6)
Extracted by 1-MN mixed with 20% IN	117 (71)		
Extracted by 1-MN mixed with 40% IN	228 (136)	279 (180)	194 (144)

Figures in parentheses are the absolute amounts of Ti eluted from raw coal, mg/kg on a mass basis of raw coal.
*Concentration of Ti in the raw IL coal.

Table 4. Concentrations of Ti in Raw WY Coal and Coal Extracts, mg/kg

	Raw Coal	Acetic Acid-Washed Coal	Sulfuric Acid-Washed Coal
Before extraction*	1160		
Extracted by 1-MN alone	5 (1)	4 (1)	<LOQ
Extracted by 1-MN mixed with 20% IN	5 (1)	7 (3)	
Extracted by 1-MN mixed with 40% IN	12 (4)	29 (17)	34 (22)

Figures in parentheses are the absolute amounts of Ti eluted from raw coal, mg/kg on a mass basis of raw coal.
*Concentration of Ti in raw WY coal.

On the consideration that Ti concentration in a coal extract could be diluted in case more organic moieties were extracted, the absolute amount of Ti (M, mg/kg, on the mass basis of coal) eluted in each run was calculated by the equation of $M = C \times Y \div (100 + A)$, where C (mg/kg, on the mass basis of coal extract) is the concentration of Ti listed in Tables 3, Y (wt%) is coal extraction yield listed in Table 2, and A the ash content (%) in coal. Values for M are shown in the parenthesis in Table 3. Attempt was further made to compare the absolute amounts of Ti eluted from different cases.

When 1-MN alone was the solvent, around 22 mg/kg Ti was eluted from the IL raw coal. Acetic acid washing caused a slight increment on Ti, which reached 31 mg/kg. Meanwhile sulfuric acid washing reduced its amount to 6 mg/kg. Addition of IN into 1-MN resulted in the great increment on the Ti elution. For instance, when 40% IN was added into 1-MN, 136 mg/kg Ti was eluted out of the raw coal. Acetic acid washing of coal led to elution of more Ti, reaching 180 mg/kg. This is in parallel to the enhancement on coal extraction yield as evidenced in Table 2, implying the association of eluted Ti with coal organic moieties. Sulfuric acid washing, however, reduced the Ti amount to 144 mg/kg. This is apparently converse to the enhancement of coal extraction yield as evidenced in Table 2.

Ti elution into WY coal extracts

WY coal has a larger amount of Ti as shown in Table 4, which is 1,160 mg/kg. Less Ti was, however, eluted out. When the raw coal was extracted, Ti has a concentration of 5 mg/kg in the extract generated by using 1-MN alone as the solvent. With the addition of polar IN into 1-MN, Ti in the resultant extracts had few change when 20% IN was added into 1-MN, which, however, reached 12 mg/kg when 40% IN was added into 1-MN.

The prior acid washing also affected the Ti concentrations. Comparisons among the Ti elution amounts (values shown in parenthesis in Table 4) make it clearer. In the case of using 1-MN alone as the solvent, around 1 mg/kg Ti was eluted from the raw coal. A prior washing of coal by acetic acid caused little change, whereas sulfuric acid washing led to the Ti concentration lower than the LOQ. When a mixed solvent containing 40% IN was used, acid washings affected the Ti elution significantly, which was improved from 4 mg/kg for raw coal extraction to 17 mg/kg for acetic acid-washed coal

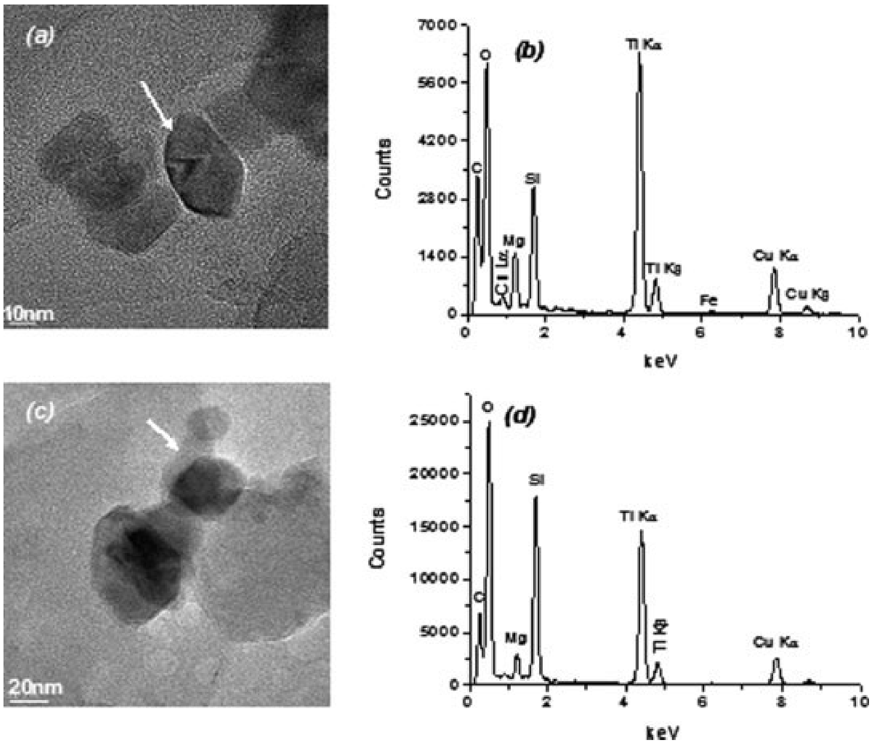

Figure 2. Ti-bearing quartz in the extract generated by extraction of sulfuric acid-washed IL coal by a mixed solvent having 40% IN. Panels (b) and (d) are the EDS results for panels (a) and (c), respectively.

Note that Cu Kα in the EDS spectra was caused by the Cu-grid support.

extraction and 22 mg/kg for sulfuric acid-washed coal extraction. Such a tendency is in parallel to the enhancement on coal extraction yield, further suggestive of the intimate association of eluted Ti with organic moieties. Moreover, it is clear that Ti in WY coal has a distinct property. Its elution behavior was apparently different to that of Ti in IL coal.

Chemical forms of Ti eluted into IL coal extracts

Few of the eluted Ti are in an ion-exchangeable form since a prior acetic acid washing caused little reduction on its elution amount. This is consistent with the fact that the bituminous coal has few carboxylic acids for attaching metallic ions. On the other hand, the eluted Ti can have two major forms in terms of their solubility in sulfuric acid.

A small amount of eluted Ti is soluble in sulfuric acid, which is the major species eluted when the nonpolar 1-MN was used alone as the solvent. Its quantity can be estimated by comparing the Ti amounts eluted from 1-MN extraction of raw coal/acetic acid-washed coal, and sulfuric acid-washed coal as shown in Table 3. Only the results obtained by using 1-MN alone were compared here on the consideration that the coal extraction yields are rather similar for these cases. As can be estimated, the sulfuric acid-soluble Ti accounts for 16–25 mg/kg on the mass basis of raw coal, having an averaged value around 21 mg/kg. Regarding its chemical form, the mineral-bound species like TiO_2 and Ti in illite/quartz are unlikely, since these two species are even insoluble in hydrofluoric acid.[22] In contrast, the Ti porphyrin is most plausible, which can be dissolved into sulfuric acid by acid cleaving the axial bonds of its tetrapyrrole ligands to coal organic matrix.[23] Study on Ti in a solvent-refined coal (SRC) also suggested the preferential association between Ti and nitrogen bonding site.[28] Nevertheless, the final evidence for this species is still lacking. A successful isolation of Ti porphyrin has not yet been reported. Even for Ti porphyrin in coal, it must undergo complicated reactions during coalification, thus, bearing little resemblance to the pure porphyrin compound in any biological materials. Further work is still necessary to establish the exact identity of this occurrence in coal.

The sulfuric acid-insoluble Ti is more significant, which constitutes the majority of Ti eluted upon IN extraction. One possibility is the small Ti-bearing mineral particles that potentially traversed the filter as noted previously. On this account, Ti in the extract of sulfuric acid-washed IL coal (1-MN added with 40% IN was used as the solvent) was observed by TEM-EDS.

As expected, the ultrafine Ti-bearing particles were detected (see Figures 2 and 3). Ti associated with quartz is one major contributor, having the size of about 10∼20 nm as evidenced in Figure 2. For a particle containing more Ti than Si, it has a quite prolonged hexagonal morphology shown in panel (a). Note that panel (b) is the elemental composition of the selected particle in panel (a). Moreover, the particle containing more Si was observed (see panels (c) and (d)), which has a slightly rhombic surface. Since quartz is very stable, these observed species should be inherently present in the parent coal, and have a fine dispersion in coal matrix. Coal fragmentation at 360°C could merely free them, while caused little change on their structures.

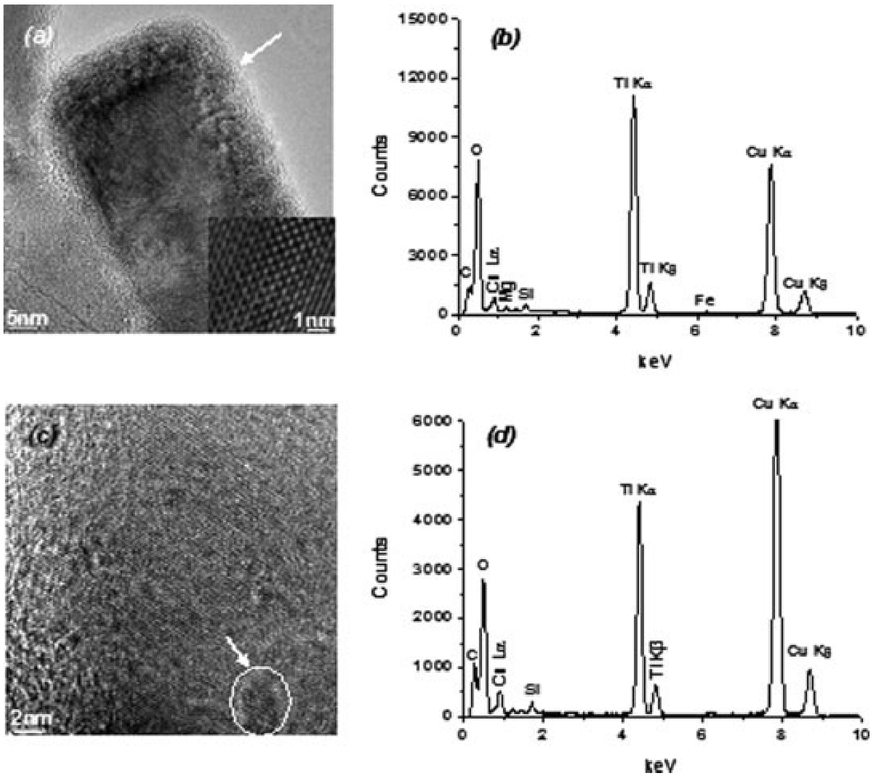

Figure 3. Titanium oxide/hydroxide particles in the extract generated by extraction of sulfuric acid-washed coal by a mixed solvent having 40% IN. Panels (b) and (d) are the EDS results for panels (a) and (c), respectively.

Cu Kα in the EDS spectra was caused by the Cu-grid support.

More strikingly, the high-purity TiO_2 nanometer-scale crystal was observed. As evidenced in Figure 3a and b, TiO_2 has a tetragonal crystalline structure. Its lattice structure as shown in inset of panel (a) was found being rhombus with an edge around 0.38 nm, which is virtually consistent with the edge of crystalline anatase that is 0.3733 nm on its tetragonal plane.[29] In addition, a further amplification indicates that this crystal is a stacking of the units around 2 nm (see the selected particle in panel (c)).

Formation of TiO_2 crystal can be explained by either a direct elution of inherent TiO_2 anatase or a conversion of organo-Ti during extraction. As suggested elsewhere,[9] anatase is one major form for TiO_2 in coals, which commonly has the size in a range of 19–26 nm. It was also found around 10 nm in the studied IL coal previously.[9] This is roughly consistent with what we observed here. Apparently, these inherent nanoparticles have the high-potential to traverse filter and concentrate in coal extract. Such a route was also proved in a study on titanium in coal liquefaction extract.[30]

Conversion of organo-Ti to anatase-like TiO_2 was confirmed by the investigations of TiO_2 deposits on coal hydrogenation catalyst. Under a hydrogen atmosphere (~6.9 MPa) at 450°C for 1 h, a chelate complex having Ti bound with phenolic O-groups on the preasphaltenes was capable of reacting with hydrogen to convert to amorphous TiO_2 and anatase.[10,31] This reaction is, however, unlikely here, since coal extraction was conducted under nitrogen protection. No hydrogen is available. In addition, investigation on the model compounds (Ti-isopropoxide, Ti-cresylate and Ti-nonylate) found that they were very unstable, and even readily hydrolyzed to TiO_2 by addition of distilled water at ambient temperature.[11] Hence, it was reasonable that, the oxygen-chelated organo-Ti compounds could rarely survive the deposition and coalification steps in the genesis of a bituminous coal deposit. For the ion-exchangeable Ti, it could also undergo decarboxylation and subsequent oxidation by water during coalification.[20] A portion of the resultant oxides can be stored in the closed pores in coal matrix, and, thus, their size is limited to a nanometer-scale. All suggest the weakness in organo-Ti conversion route. In contrast, the sulfuric acid-insoluble Ti can be solely attributed to inherent nanometric anatase and Ti associated with quartz. Few organo-Ti except 21 mg/kg Ti porphyrin could be present in this coal.

Variation of the elution amounts of these nanometric particles with coal extraction yield was further investigated. As explained earlier, the sulfuric acid-soluble Ti accounts for ~21 mg/kg on the mass basis of the raw coal. Accordingly, the quantity of sulfuric acid-insoluble fraction of Ti in each extract (except those produced by extracting sulfuric acid-washed coal) can be calculated by subtracting aforementioned value from the eluted total Ti. The results are plotted as a function of coal extraction yield in Figure 4. Interestingly, few of the Ti-bearing nanoparticles could be released at a coal extraction yield of ~40% obtained by using 1-MN alone as the solvent. Adding IN into 1-MN gave rise to a rapid increment on Ti elution, which even has a rate higher than that of the organic moieties. This strongly indicates that

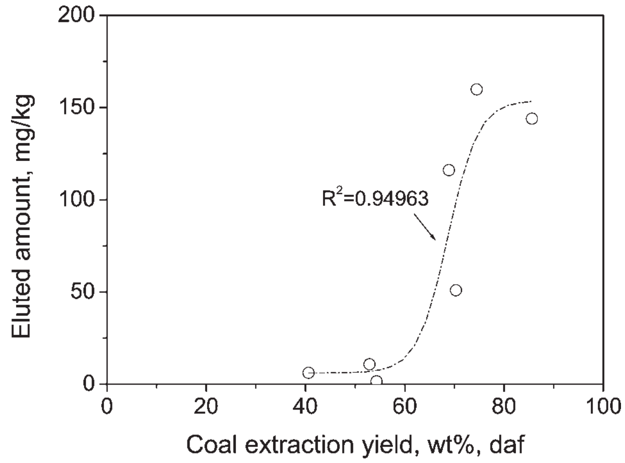

Figure 4. Variation of sulfuric acid-insoluble Ti elution amount with IL coal extraction yield.

these nanoparticles are not distributed uniformly throughout the organic matrix of IL coal. They are preferentially enriched in the IN-extractable moieties that have high-polar property in the raw coal. Only the polar solvents can mobilize them. In addition, Figure 4 shows that the sulfuric acid-insoluble Ti elution leveled off after the coal extraction yield reached ~80%. Conceivably, these nanoparticles have a maximum sum around 144–160 mg/kg in IL coal. As to the remaining Ti in the raw coal, it can be assigned as coarse mineral compounds which are larger than 0.5 μm in diameter.

In summary, the compositions of Ti-bearing species in IL raw coal are tabulated in Table 5. In terms of solubility in organic solvents, Ti in this coal has three major forms, Ti porphyrin which is truly soluble, Ti-bearing nanoparticles (anatase and Ti associated with quartz) that can traverse the filter for isolating coal extract, and coarse mineral particles larger than 0.5 μm. The former two has lower percentages, but their behavior upon coal extraction is much important, having a high-potential to transfer into coal extract as evidenced in this study.

Chemical forms of Ti eluted into WY coal extracts

As proven in Table 4, Ti eluted upon extractions of this coal is insoluble in each acid. Here again, the carboxyl-bound Ti ion plays little role. This is consistent with what reported for other metals in coal-derived liquids.[12] Such a phenomenon can be explained by few of carboxylic-Ti in this low-rank coal. No sulfuric acid-soluble Ti was found as well, suggesting few of the Ti porphyrin in this coal.

Regarding the sulfuric acid-insoluble Ti, the nanoparticles of either anatase or Ti associated with quartz are reasonable as well. Nevertheless, the possibility for the presence of Ti chelates cannot be ruled out. Compared to the mature bituminous coals, the subbituminous coal has a large amount of oxygen-containing functional groups to attach metallic ions. As suggested previously, Ti in subbituminous coals has a large fraction associated with phenolic-O ligands.[10] In such a case, Ti can be embraced tightly in an organic moiety to form a configuration that is hardly attacked by any acids, while is reasonably extracted by a polar solvent. It is difficult for us to distinguish its form due to its low concentration.

Table 5. Proposed Ti-bearing Species Compositions in IL Bituminous Coal

Ti-bearing Species	Characteristics	Amount, mg/kg
Ti porphyrin	Soluble in sulfuric acid (7%, v/v in methanol) and extractable by 1-MN alone	15~25
Ti-oxide/Ti-Si nanooxides embedded in nonpolar fraction of IL coal	Insoluble in sulfuric acid and extractable by 1-MN alone; relatively crystalline; and have a size around 10–20 nm.	~6
Ti-oxide/Ti-Si nanooxides embedded in polar fraction of IL coal	Insoluble in sulfuric acid and extractable by polar indole, relatively crystalline; and have a size around 10–20 nm.	144~160
Coarse Ti-bearing minerals	Insoluble in sulfuric acid and not extractable by solvents; discrete particles having a size >0.5 μm	694~720

Similar to the IL coal case, elution of the sulfuric acid-insoluble Ti in WY coal is also prominent upon IN extraction (see Figure 5). Here again this suggests a preferential distribution of these species in the polar fraction of this coal. Since <25 mg/kg Ti was eluted at the coal extraction yield of ~70%, the organic fraction embracing Ti in WY coal should be much more resistant to the solvents employed here, possibly due to a highly crosslinked macrostructure for this low-rank coals.

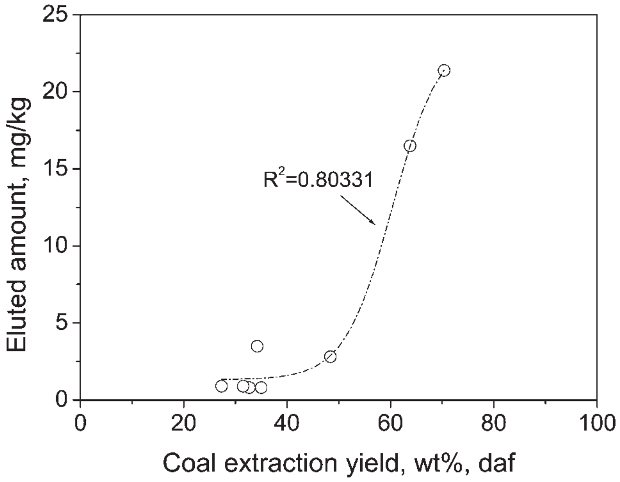

Figure 5. Variation of sulfuric acid-insoluble Ti elution amount with WY coal extraction yield.

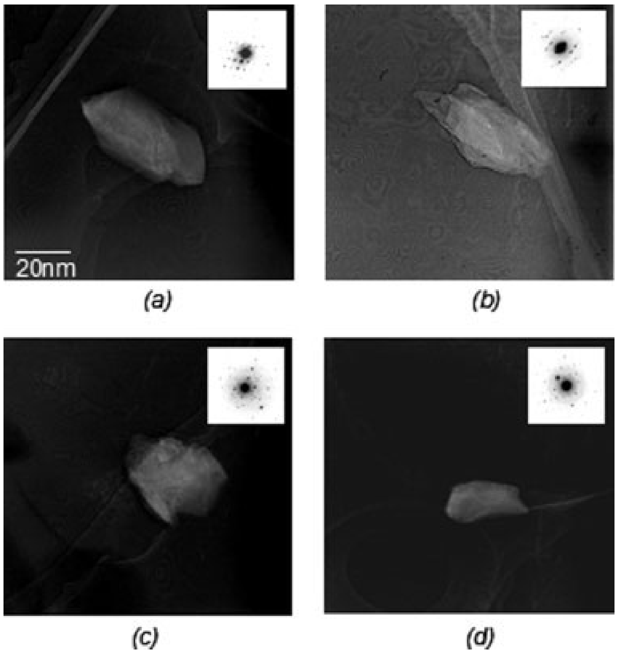

Figure 6. Nanometer-scale Ti-bearing particles from combustion of IL coal extract at 1,000°C.

Photographs (a)–(d) are anatase, rutile, brookite-like crystalline and $FeZnTiO_4$, respectively.

Ti-bearing fly ash generated from the combustion of coal extract

The Ti-bearing particles in the IL coal extract combustion-derived fly ash have a size up to 20 nm. Four typical morphologies are illustrated in Figure 6. A rod-like morphology was observed, having a prolonged hexagonal facet as shown in panel (a). Matching of its electron crystalline pattern (see the inset) indicates an anatase-like compound (PDF 21-1272). Panel (b) shows the rutile (PDF 21-1276) with an irregularly rod-like shape. A crystalline nanoparticle having a rather hexagonal shape is shown in panel (c), exhibiting an electron crystalline pattern close to that of brookite (PDF 46-1237). Moreover, a distorted rod-like shape was observed (see panel (d)), which is similar to $FeZnTiO_4$ (PDF 35-1373). The following reaction pathways may apply to their formation

$$\text{Ti} - \text{porphyrin} \xrightarrow{\text{decomposition}} \text{Ti(g)} + \text{O}_2\text{(g)} \rightarrow \text{TiO}_2\text{(s)} \quad (1)$$

$$\text{TiO}_2\text{(s, anatase)} \rightarrow \text{TiO}_2\text{(s, rutile)} \quad (2)$$

$$\text{TiO}_2\text{(s, anatase)} + \text{Zn(g)} + \text{FeO(s)} \rightarrow \text{FeZnTiO}_4\text{(s)} \quad (3)$$

Reaction (1) could initiate with the decomposition of Ti-porphyrin at a low-temperature. Subsequently, the resulting Ti vapor was oxidized and condensed into nanooxides having a variety of crystalline structures as shown in panels (a)–(c). The conversion of inherent anatase to rutile, as suggested in reaction route (2), should occur as well. It is thermodynamically available at temperatures >700°C.[17] In addition, the route (3) indicates that the inherent TiO_2 (anatase) could in part react with Fe-bearing species and gaseous Zn to form a complex compound. This finding is in agreement with the fact that the submicrometer-sized TiO_2 is one effective sorbent for capturing metallic vapors during coal combustion.[32] Due to the deposition of metals on its surface, the crystalline structure of TiO_2 (anatase) was deteriorated to a certain extent (see panel (d)). Regarding the behavior of Ti during WY coal extract combustion, it should follow the aforementioned routes, as well as one involving the crystallization of Ti chelate. Accordingly, TiO_2 polymorphs could be formed as well. These reaction routes can also explain the emission of nanometric rutile crystals from the combustion of raw coal.[33]

Implications of the findings in this study

The combination of prior acid washing and solvent extraction provided in-depth understandings on the mode of occurrence of Ti in two U.S. coals, as well as in coal extracts. Although the final evidence is lacking, the organo-Ti possesses different coordination states in the different coals. Ti porphyrin is the most likely species in the studied IL bituminous coal, which is soluble in both sulfuric acid (7% in methanol, v/v) and a nonpolar solvent like 1-MN. On the other hand, the organo-Ti in the studied WY subbituminous coal mostly involves the coordination of Ti ion with the oxygen-containing polar functional groups such as phenolic hydroxyl. Similar to other organometals, these two species should be adsorbed from the biological precursors like plants and vegetables at the initial stage of coalification.[15] Ti porphyrin might be the surviving fragments of the original protein; meanwhile Ti chelated with oxygen can become more complicated due to its crosslinking with other organic moieties. Moreover, it can in part undergo oxidation to form free oxides, or those incorporated into clay minerals.[20] The resulting particles are in part stored in the closed voids of coal matrix, having a nanometer-scale size. Quantities for these species are first reported in this study. The conventional methods for determining the modes of occurrence of trace metals in coal, e.g., sequential acid leaching,[34] usually give little information for organometals, and the mineral particle sizes as well.

Organo-Ti and nanometric particles are preferentially eluted into coal extracts. To achieve a coal extraction yield around 50%, Ti in the resulting extracts can reach ~46 mg/kg for IL extracted by 1-MN alone and ~7 mg/kg for acetic acid-washed WY coal extracted by 1-MN added with 20% IN (see Tables 3 and 4), respectively. Since the overall inorganic elements in these two extracts have a sum of 807 and 330 mg/kg, respectively, elution of Ti is less significant compared to other metals. In addition, as shown in Figure 6, the Ti-bearing particles derived from combustion have a mean size smaller than 20 nm, which are too small to cause erosion on a turbine blade.[8] Nevertheless, to obtain a higher coal extraction yield, the eluted Ti will be increased rapidly. Approximately 200 mg/kg Ti can be present in the IL coal extract having a yield of ~80% (see Table 3). In this case, its impact on gas turbine operation must be cared. Its elution needs a control as well. In contrast, for WY coal extract having a yield around 70% (generated by extracting the sulfuric acid-washed coal by 1-MN mixed with 40% IN), only 34 mg/kg Ti is present within it. Less of other metals were found as well. All suggest that the extract of acid-washed WY coal is much benign for the gas-turbine combustion system.

The results obtained in study are also helpful for management on the risks relating to Ti during coal utilization. When coal extract is combusted, the resultant ultrafine particles have a large number concentration, and readily escape any conventional pollution control devices as well. Hence, it should be of environmental concern. For instance, the nutritional balance in ecological systems is likely influenced if TiO_2 deposits into water or soil. The ultrafine TiO_2 is also respirable to the livings. Its inhalation can incur great lung inflammation due to its interaction with cells to generate free radicals.[35,36] All highlight the significance on further studying the environmental issues relating to TiO_2 nanoparticles derived from coal combustion.

Conclusions

The elution behavior of Ti upon solvent extraction, as well as its transformation during combustion has been investigated in the cases of two APCS coals. The major conclusions are drawn from the following:

1. The elution of Ti varied with both coal type and solvent polarity greatly. For the extraction of bituminous IL coal, employing 1-MN alone could lead to about 46 mg/kg Ti in its extract, compared to 228 mg/kg Ti in the extract generated by adding 40% polar IN into 1-MN. For the subbituminous WY coal, less Ti was eluted. Only 34 mg/kg Ti was found in its extract having a yield around 70%.
2. The eluted Ti upon IL coal extraction is composed of Ti porphyrin that is truly soluble in a solvent, and nanometric anatase and Ti associated with quartz that could traverse the filter for isolating coal extract. The former was preferentially extracted by the nonpolar 1-MN alone. On the other hand, the nanoparticles were preferentially eluted when the polar IN was employed, due to their association with the polar fraction of this coal. On the mass basis of raw coal, Ti porphyrin accounts for 16–25 mg/kg. The Ti-bearing nanoparticles have a sum around 144–160 mg/kg, while the remaining coarse particles have a sum of 694–720 mg/kg.
3. The eluted Ti upon WY coal extraction is solely sulfuric acid-insoluble fraction. It can include nanoparticles and Ti chelates stored in polar coal fractions as well. The ion-exchangeable Ti played little role.
4. Ti in coal extract could transform into TiO_2 polymorphs and complex compound at 1,000°C. These species have a mean size around 20 nm or less. The risk relating to gas turbine blade erosion is weak. Nevertheless, these fine particles should be of environmental concern since they can escape the conventional pollution control devices.

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