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Acoustic Treatment of a Coal Gasification Residue for Extraction of Selenium

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The present study demonstrates that acoustic treatment of a coal gasification residue in water with dissolved CO_2 is an effective route for extracting selenium (Se). It was recently revealed that the acoustic treatment can enhance the extraction of a series of metals, Na, K, Ca, and Si, from carbonaceous structures, e.g., biochar, as a result of the cavitation-induced phenomena, including generation of microjets, shock waves, and hot spots. Ultrasound (US) irradiation of graphitic carbonaceous structures in water/CO_2 partially exfoliates the graphitic clusters, creates new pores, opens the blocked pores, and increases the internal surface area, carbon content, and hydrogen content through a group of sonolysis reactions of CO_2 and H_2O.[1,2] The present study used US treatment with different amplitudes and total US energy consumption or irradiation durations under a CO_2 blanket in the headspace of the solution to determine the extraction of a series of heavy metals, including selenium, from a coal gasification residue. The experimental results (not yet optimized) showed a significant reduction in selenium content (71%) in treated samples at 2000 J and 50% US amplitude. A thorough study of this approach is certainly warranted.

The coal combustion and gasification residues typically contain toxic heavy metals, including arsenic, lead, mercury, cadmium, chromium, selenium, etc., causing cancer, pulmonary disorder, cognitive defects, developmental delays, and behavioral problems.[3] A coal gasification residue is a major waste stream from the power plants, which is often stored in landfills as a long-term disposal mean.[3] A typical concern regarding the landfills involves the risk of catastrophic failure (such as impoundment of ponds containing a coal ash slurry), groundwater contamination, and their hazardous non-reversible effects on the local environment, especially with selenium. The major environmental implication of selenium is its propensity to accumulate in aquatic food chains, endangering human lives.[4] No satisfactory chemical, physical, or biological treatment exists to remove selenium, because the existing treatments can only work on a small scale and are inefficient and expensive for a large scale.[5]

Acoustic treatment of biochar has been considered a new route for the production of advanced sorbents for CO_2 capture[6] and adsorption of heavy metals in wastewater.[7] The residue used in the current study was obtained from a coal gasifier in China. It was derived from lignite and has an unusually high carbon content, 20.6%, representing a significant fraction of unused energy. The company is currently storing the residue in a landfill. In the current study, the acoustic energy was applied to the mixture of 7.5 g of residual powders in 125 mL of water saturated with CO_2.[2] The US treatment was conducted with a QSonica Q700 sonicator of 20 kHz and 700 W in the presence of 7% CO_2 in headspace. To control the CO_2 concentration at 7%, a mixture of CO_2 (50 mL/min) balanced with helium (664 mL/min) was blown into the headspace of the solution. The following US amplitude and energy were chosen to evaluate their effects on mineral leaching: 5% US amplitude and 2000 J energy (US-A5%-E2000J), 50% US amplitude and 2000 J energy (US-A50%-E2000J), and 50% US amplitude and 4000 J energy (US-A50%-E4000J). The change of electrical energy into mechanical energy in the US transducer causes its tip to move up and down. The displacement of the US tip is called its amplitude, and this is adjustable. In this work, an US tip with the amplitude of 120 μm was used (amplitude of 100%). Therefore, at settings of 50 and 5% amplitude, the probe will achieve the amplitudes of approximately 60 and 6 μm, respectively. A QSonica Q700 sonicator is equipped with a monitor, which shows the amplitude and total amount of electrical energy. Furthermore, ultrasonication for 1800 s was employed at 50% amplitude as well to assess the effect of a prolonged acoustic treatment. To illuminate the impact of US irradiation, the leaching of metal was studied with water washing for 167 and 1800 s without irradiation. The durations were selected on the basis of experiments with 5% amplitude and 2000 J energy and 50% amplitude and 1800 s, respectively. After each treatment, the mixture was filtered and the residue was dried at 60 °C overnight under vacuum and analyzed for mineral and organic changes as well as elemental compositions and metal removal.

EFFECTS OF US AMPLITUDE, ENERGY, AND IRRADIATION DURATION

Table 1 depicts the role of acoustic treatment in the extraction of heavy metals. Leaching of selenium, sodium, and potassium was accelerated when the US amplitude was increased from 5 to 50% (at a constant US energy of 2000 J). The calculations of this study are based on "weight change" and not direct subtraction. In this method, the overall mass change of the carbonaceous structure during treatment is taken into account. For example, US-A50%-E2000J treatment showed a weight loss of 22.78% (or weight change of −22.78%) (Table 2). Now, percent removal can be calculated as

$$\frac{[(1+\mathrm{WC})(C_{\mathrm{ash}}\text{ of TR})(C_{\mathrm{Se}}\text{ of TR})]-[(C_{\mathrm{ash}}\text{ of RR})(C_{\mathrm{Se}}\text{ of RR})]}{(C_{\mathrm{ash}}\text{ of RR})(C_{\mathrm{Se}}\text{ of RR})}\times 100 \tag{1}$$

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Table 1. Changes in the Elemental Metal Concentration of the Residue upon Treatment (Weight-Based Calculation)[a]

sample description	Na (μg/g)	Cd (μg/g)	Se (μg/g)	K (μg/g)	Ca (μg/g)	As (μg/g)	Hg (μg/g)	Cr (μg/g)	Pb (μg/g)
raw	10900	0.66	2.6	13400	43000	7.7	<0.02	98	80
US0-A0-W167s (water washed)	11000	0.8	2.5	14400	43900	3	<0.02	97	80
change during treatment (%)	−26	−11	−29	−74	−21	***−71***		−27	−26
US0-A0-W1800s (water washed)	10800	0.8	2.5	14100	42500	2	<0.02	95.8	85.6
change during treatment (%)	−26	−9.2	−28	−21	−26	***−80***		−27	−27
US-A5%-E2000J	10650	0.64	2.25	13350	41950	7.7	<0.02	96	79.5
change during treatment (%)	−26	−25	−33	−23	−26	−24		−25	−24
US-A50%-E2000J	10200	0.6	1	13300	43000	8.4	<0.02	105	79.3
change during treatment (%)	**−30**	−17	***−71***	**−25**	−25	−18		−19	**−25**
US-A50%-E4000J	10400	0.6	1.3	13400	43800	8.7	<0.02	110	83.9
change during treatment (%)	−29	−32	**−63**	−26	24	−16		−17	22
US-A50%-E62977J	11000	0.8	2.4	14400	44400	3	<0.02	96	84.7
change during treatment (%)	−24	−9	−30	−19	−22	−71		−26	−20

[a] Change in the metal concentration was calculated taking the weight change into consideration during treatment. The maximum possible selenium removal was achieved at 50% US amplitude and 2000 J US energy consumption within 41 s. A total of 80% of arsenic was soluble in water for 1800 s, implying the risk of leaching of metals in water.

Table 2. Treatment of Residue: Treatment Conditions and Changes in the Biochar Weight, pH, Mineral Content, and Organics[a]

parameter	raw	US0-W167s[b]	US0-W1800s[b]	US-A5%-E2000J[c]	US-A50%-E2000J[b]	US-A50%-E4000J[b]	US-A50%-E62977J[b]
mass of residue (res) used in the sonication (g)		7.5	7.5	7.5	7.5	7.5	7.5
pH of water		6.92	6.91	6.34	6.85	6.92	6.95
water volume used (mL)		125	125	125	125	125	125
pH of H_2O + res		7.83	7.8	8.12	7.77	7.81	7.83
pH of H_2O + res + CO_2		4.9	4.94	4.98	4.92	5.07	4.84
amplitude of sonication (%)				5	50	50	50
CO_2 in headspace (%)				7	7	7	7
U.S. energy consumed (kJ/g)				0.25	0.25	0.55	8.4
U.S. energy consumed (kcal/g)				0.06	0.06	0.13	2
maximum temperature (°C)				26	25	28	32[d]
treatment time (s)		167	1800	167	41	80	1800
pH of filtrate		5.79	5.81	6.88	6.51	6.71	7.14
weight change (%)		−23.43	−22.18	−22.4	−22.78	−23.55	−21.75
ash content (%)	80.3	77.17	77.28	78.9	78.36	77.96	77.5
mineral change (%)		−26.41	−25.11	−23.75	−24.65	−25.03	−24.48
organics (%)	19.7	22.83	22.72	21.1	21.64	22.04	22.5
organic change during treatment		−0.44	−0.39	−0.66	−0.59	−0.56	−0.41

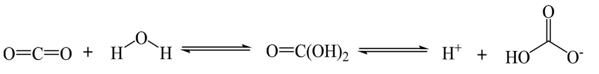
[a] Percent weight change, percent ash content, and percent mineral change are proportional to the US energy consumed. US, ultrasound; A, amplitude (%); E, ultrasound energy supplied (J); and W, water washed (s). [b] Performed with distilled water. The source of deionized water gave fluctuating pH values after the initial experiments were performed, and therefore, the subsequent experiments were conducted using distilled water, which demonstrated more stable pH values. [c] Performed with deionized water. [d] Temperature was controlled using an ice bath.

where WC, TR, RR, C_{ash}, and C_{Se} denote the weight change, treated residual, raw residual, ash content, and selenium content, respectively. A similar calculation was used for the other metals including arsenic.

Se removal increased from 33% for US-A5%-E2000J to 71% for US-A50%-E2000J. This behavior can be explained as a function of acoustic cavitation intensity, which increased significantly at high amplitude, accelerating the mass transfer. This facilitates the leaching of minerals that have strong bonding with the carbonaceous support. Meanwhile, the removal of cadmium and chromium was reduced with US amplitude. This may be due to the formation of agglomeration of metal as a result of fusion at a high temperature as a result of intensified sonication.[8] A similar behavior was observed when greater acoustic energy (4000 J) was applied at the same amplitude (50%). The results showed 12% reduction in Se and 2% in Cr removals, when the energy increased from 2000 to 4000 J. On the contrary, Cd removal was almost doubled with increasing acoustic energy. These results suggest that optimizing the interaction of US energy and amplitude can further improve the removal of target heavy metals. On the contrary, Cd removal was almost doubled with increasing acoustic energy. This necessitates a thorough analysis of the interaction between the kinetics of leaching of different minerals with acoustic intensity. In the next step, the effect of ultrasonication duration was investigated by treating the residue sample for a longer duration (1800 s) at 50% amplitude. Data in Table 1 suggest that a longer duration does not enhance the leaching of heavy metals, which could be attributed to aggregation during the long treatment time.[9]

■ EFFECT OF DISSOLVED CO_2

Dissolved CO_2 is the main source of water acidity in the system of interest. CO_2 keeps entering water through its interface with the atmosphere. Water reacts with aqueous CO_2 (aq), forming carbonic acid. Dissolved CO_2 in the form of carbonic acid may lose protons to form bicarbonate (reaction R2; $K = 2.00 \times 10^{-4}$) and carbonate ($K = 4.69 \times 10^{-11}$).[2]The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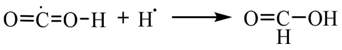
generated H^+ ions interact with the metallic ions present in the residue sample through ion exchange and remove them from the structure. This phenomenon contributes in hydrogen uptake as well. Moreover, sonolysis of CO_2 in water yields acidic organics, including formaldehyde and formic acid, in the following way. It is known that US splits water to form hydrogen and hydroxyl radicals (reaction R3). On the other hand, several studies showed the sonolysis of CO_2 in aqueous solution.[10−12] Henglein et al.[12] revealed that CO_2 plays two major roles: scavenging hydrogen radicals and decomposition to CO. CO_2 scavenges $^{\bullet}H$ from the sonolysis of water to form $^{\bullet}COOH$, which is followed by the formation of a small quantity of formic acid (reactions R4 and R5). Formaldehyde can then be formed as the byproduct of HCOOH degradation (reactions R6 and R7).[13] More details can be found in our previous work.[2]

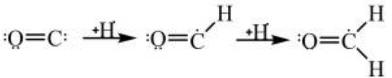
$$\mathrm{H{-}OH} \rightleftharpoons \mathrm{H}^{\bullet} + \mathrm{OH}^{\bullet} \qquad (3)$$



$$\mathrm{O{=}\dot{C}{=}O{-}H} + \mathrm{H}^{\cdot} \longrightarrow \mathrm{O{=}\underset{H}{C}{-}OH} \qquad (4)$$

$$\mathrm{O{=}C{=}O} + \mathrm{H}^{\bullet} \rightarrow \mathrm{O{=}C{=}O{-}H} \qquad (5)$$

$$\mathrm{O{=}\underset{H}{C}{-}OH} + \mathrm{OH}^{\cdot} \longrightarrow \mathrm{O{=}\dot{C}{=}O{-}H} + \mathrm{H{-}O{-}H} \qquad (6)$$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These compounds could react with graphitic carbonaceous structures containing Lewis base and π electrons. The basic nature of the residue in water increased alkalinity, which helped to trap a higher amount of CO_2 and organic acids during CO_2 bubbling and treatment and, thus, enhanced the removal of basic cations through ion exchange and acid/base reactions.

■ EFFECT OF WATER WASHING

The heavy metals are partially soluble in water. Hence, the water-washing tests were conducted to illuminate the impact of US treatment. As observed, 29% of Se was leached out of the residue by simple washing. The value increased to 71% using a short term of US irradiation under a CO_2 blanket. Therefore, enhanced removal of selenium through acoustic cavitation serves as a viable treatment technique for overcoming the challenges of handling coal-fired residues. Dissolved selenium (selenite or selenate) can be further removed from the wastewater through either biological or chemical/physical processes. In the former, dissolved selenium can be biologically reduced by bacteria under anoxic conditions to elemental selenium.[14] The latter technologies include oxidation/reduction, iron co-precipitation,[15] ion exchange, and adsorption.[16] On the other hand, arsenic exhibited easy percolation during water washing. As observed, 80% of arsenic that was removed from the residue was water-leachable as reported earlier.[17] Therefore, integration and optimization of water and ultrasonic washing can effectively remove a wide range of metals, particularly As and Se, which can induce plant toxicity and subsequent effects on animals and humans.[17]

■ IMPLICATIONS OF MINERAL AND ORGANIC CHANGE DURING TREATMENT

The various parameters involving in the acoustic treatment process and their changes along with elemental compositions are reported in Tables 2 and 3. Weight change (in Table 2) represents a combination of mineral leaching, organic leaching, and fixation of organics and minerals on the graphitic carbonaceous structure (herein residue) during the treatment. All weight changes show negative values, indicating that the acoustic treatment induced a weight loss through the removal of inorganics or minerals and a small amount of change in organic compounds.

The weight loss was more pronounced with increasing the ultrasonic amplitude and energy. This trend was also observed in our previous studies.[1,2] In addition, the observed trend of weight loss is consistent with the percent ash reduction and mineral leaching (Table 1). As a result, an increase in sonication amplitude (from 5 to 50% at a constant energy consumption of 0.06 kcal/g) and energy (from 0.06 to 0.13 kcal/g) enhanced the mineral loss from 23.75 to 25.03%.

Table 3. Elemental Compositions of the Raw and Treated Residues (Dry Basis)

sample	C (wt %)	H (wt %)	N (wt %)	O[a] (wt %)	S (wt %)	ash (wt %)
raw	20.6	0.17	0.11	7	0.69	78.54
US0-A0-W167s	20.64	0.33	0.11	4.45	0.57	78.28
change during treatment (%)	−23	49	−23	−51	−37	−23
US0-A0-W1800s	20.62	0.33	0.12	3.71	0.6	78.49
change during treatment (%)	−22	51	−22	−59	−32	−22
US-A5%-E2000J	21.52	0.17	0.11	6.42	0.7	78.39
change during treatment (%)	−19	−22	−22	−29	−22	−22
US-A50%-E2000J	20.65	0.19	0.08	6.22	0.62	78.63
change during treatment (%)	−22.4	−14	−44	−32	−31	−23
US-A50%-E4000J	19.9	0.18	0.08	5.99	0.62	78.14
change during treatment (%)	−26	−19	−44	−26	−31	−24
US-A50%-E62977J	20.37	0.35	0.11	3.31	0.69	78.63
change during treatment (%)	−22	61	−22	−63	−31	−21

[a] Oxygen content was calculated by the “direct method”.

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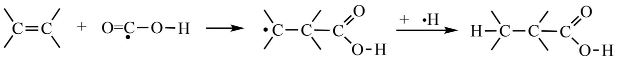
The organic content is a measure of the combustible (i.e., gasified) fraction of the residue, such as percent C, percent H, percent O, percent N, and percent S contents. The change in organic composition during the treatments has been calculated and reported in Table 3. The highest hydrogen fixation was observed in water-washed samples, while a slight H increase was obtained in ultrasonic-treated samples. This is attributed to the different types of minerals removed and the kinetics of removal. The gain in hydrogen content of water-treated samples suggested the attachment of the H^+ ion through ion exchange, $\overline{M}^+ + H^+ \leftrightarrow \overline{H}^+ + M^+$; however, removal of mineral compounds under US irradiation is most likely due to cavitation and its implications.

On the other hand, the reduction in O and C contents of samples treated with US is significantly lower compared to the water-washed residue. Because the weight loss is a combination of mineral leaching, organic leaching, and fixation of organics and given the fact that the values of ash loss in both US and water-treated residues are very close, data in Table 3 imply significant losses of both organic contents (C and O) during water washing. Nevertheless, US appears to reduce these losses and possibly induces C and O fixation. Generally, 19 complicated reactions occur in sonolysis of pure water alone, generating a series of highly reactive species and radicals, including $H^\bullet$, $^\bullet OH$, H_2, $^\bullet HO_2$, O_2, H_2O_2, $O^\bullet$.[18] On the other hand, CO_2 and H_2O are the only sources for C, O, and H fixation on the residue. Because an initial sonochemical reaction is the addition of $H^\bullet$ to CO_2 to form a carbon-centered $^\bullet COOH$ radical, it is possible that the radical adds to a π bond and the resulting radical combines with another radical, giving a carboxylic acid (reaction R8).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Sonolysis of dissolved CO_2 can also directly split CO_2 to form highly reactive $^\bullet O^\bullet$. Diradical oxygen initiates a chain of reactions to form $\dot{O}_2$, a carbon atom, and CO. Formic acid and formaldehyde may also be fixed on the residue that causes an increase in C. We remain interested in the possible fixation of carbon from CO_2 to the graphitic carbonaceous structure.[2] Additionally, the infrared (IR) spectrum shown in Figure 1 represents the spectrum of raw and activated residuals under different conditions. The overall shape of the spectra remains the same, except the C−O peak at 1100 cm^{-1}.[1] The figure shows that the intensity of the C−O peak (which comes from ether linkage) increased for activated samples with enhancing the sonication amplitude and energy. The peak is ascribed to alkoxy group (ether) stretching, and the increase in intensity can be explained as a result of the interaction between C−O and CO_2.[19]

This study introduced a fast and economically feasible method for removal of selenium from coal combustion and gasification residues in a water/CO_2 system under US irradiation. The process was applied at room temperature and effectively removed 71% Se within 41 s. Additionally, the study revealed that simple water washing dissolved with CO_2 can remove a significant amount of arsenic (80%) from the residue samples. The results suggested that integration and optimization of ultrasonic treatment of different acoustic amplitudes (5−50%) with simple water washing can maximize the removal of a wide range of heavy metals of the residual. The results were obtained at an early stage of our study; thus, it needs further thorough investigation to optimize the process, aiming at maximum removal of all of the heavy metals.

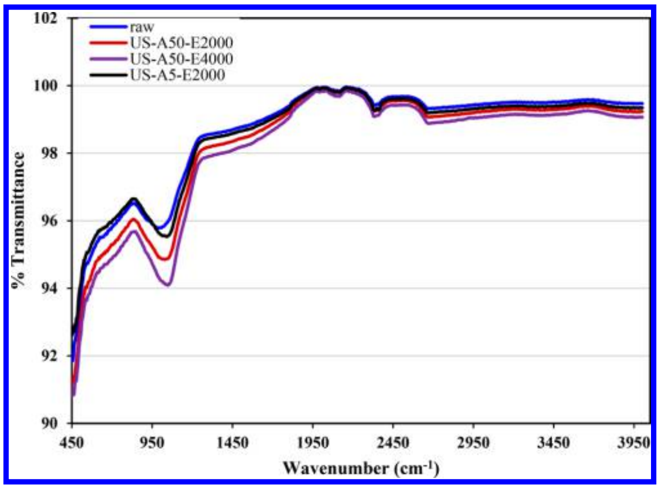

Figure 1. Fourier transform infrared (FTIR) spectra of raw and treated samples are shown. The sample treated under 5% amplitude and 2000 J energy is denoted as US-A5-E2000; the sample treated under 50% amplitude and 2000 J energy is denoted as US-A50-E2000; and the sample treated under 50% amplitude and 4000 J energy is denoted as US-A50%-E4000.

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Notes

The authors declare no competing financial interest.

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