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Heavy Metals in Colorado and Chinese Oil Shale Semicoke: Disposal Issues, Impediments to Byproduct Conversion

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ABSTRACT: Oil shale, a fine-grained sedimentary rock, contains a proportionally large amount of kerogen, which can be converted into oil by thermal degradation of the compacted rock. The primary byproduct of current oil shale oil extraction processes is semicoke. Its landfill deposition presents a possible threat to the environment and represents a waste of a potentially useable byproduct. In this work, we explore the heavy metal content of oil shale semicoke pyrolyzed at 500 and 1000 °C to better understand the risks posed by disposal of oil shale processing waste on the nearby environment, as well as impediments to potential byproduct conversion. The greatest potential obstruction to byproduct conversion and the greatest environmental risk posed by open air disposal of oil shale semicoke is likely due to relatively high arsenic concentrations; using X-ray fluorescence spectroscopy, we find arsenic concentrations in semicoke (pyrolyzed at 500 °C) ranging from 25 ppm for Chinese oil shale from the Huadian mine (class C) to 79 ppm for Green River, Colorado, 50 gallons per ton (GPT) of oil shale. Other heavy metal elements analyzed, including barium, copper, lead, manganese, and iron, are well below the United States Environmental Protection Agency (U.S. EPA) regional screening limits.

1. INTRODUCTION

Over the past several decades, concerns over dwindling fossil fuel resources have prompted a surge in research and development of alternative energy technologies. Although scientists, politicians, and ordinary citizens alike agree with the need to develop new energy generation technologies, the choice among specific alternative energy sources available is a hot topic for debate. In North America, where tar sand and oil shale deposits are vast, experimentation is ongoing in the areas of alternative fossil fuels. Oil shale is a low-grade solid fuel with high ash content. A fine-grained sedimentary rock, oil shale contains a proportionally large amount of kerogen, which can be converted into oil by thermal degradation of the compacted rock.

Worldwide deposits of oil in shale are estimated at upward of 2.8 trillion barrels of recoverable oil.[1,2] Historically, the cost of oil produced from oil shale is markedly higher than that of conventional oil processes, such as drilling, and this has inhibited countries, such as Australia and the United States, from developing an oil shale industry.[3] Interest in oil shale in the United States was piqued in the 1970s when the price of oil peaked. However, when oil prices fell, research toward oil production from shale markedly decreased. However, with oil prices once again setting record highs, oil shale is back at the forefront of many discussions as a stopgap fossil fuel source between our reliance on the pipelines of the Middle East and a renewable energy future.

There are several barriers to commercial use of oil shale as a domestic source for oil. These include overcoming process water requirements and ground swelling issues, long-term stability of the manufactured oil, and dealing with the veritable mountains of oil shale semicoke produced.[4,5] This paper addresses the latter issue. The two primary utilization pathways for oil shale are electricity generation by power stations and oil production.[5] Electricity production generates ash as the primary waste, a silica-based powder with little to no volatile organics present, as the compacted rock is burned directly in a combustion chamber. Oil extraction from oil shale creates semicoke as a byproduct via pyrolysis of the shale rock to extract the oil. In this scenario, the rock is compacted to increase the available surface area (to increase oil yield) and heated upward of 500 °C under an inert gas to prevent oxidation and combustion of the fuel while extracting the oil. The oil yield primarily depends upon the amount of kerogen originally present in the shale, as well as the pyrolysis temperature. Whereas ash from electricity generation has low carbon content (less than 0.1% by mass of solid material), semicoke has a relatively high amount of organic char present, depending upon the aforementioned shale and extraction conditions.

Previous work shows that oil shale semicokes have relatively high overall surface areas despite a 2−18% organic char fraction (and thus have high specific surface areas, upward of 300 m^2 g^{-1}, unactivated), leading us to posit a potential use of oil shale semicoke as a sorbent material.[6] Similar to conventional fossil fuels, oil shale is a mixture of inorganic and organic compounds formed during prehistoric times. It is these inorganic compounds that lead us to question whether heavy metals present in the oil shale rock remain within the semicoke after processing. This is a potential impediment to using the semicoke as an *in situ* sorbent. If there are a sufficient amount of metals present, the semicoke may require extensive pretreatment and nullify the byproduct

conversion benefits of disposal cost reduction and environmental mitigation. The presence of heavy metals represents a potential issue to the open-air disposal of the semicoke, because these metals could leach into groundwater and transport through the environment. Fathoni et al. note that issues of semicoke storage and disposal surpass concerns over the stability of extracted oil.[4] By investigating a variety of oil shale semicoke samples from China and the United States, we probe the feasibility of waste-to-byproduct conversion of semicoke, as well as storage and disposal issues because of entrained heavy metals as a function of the shale origin and pyrolysis temperature.

Prior studies document the presence of heavy metals in oil shale fly ash. In some parts of China, for example, studies demonstrate an accumulation of lead, cadmium, zinc, thallium, barium, and arsenic in oil shale fly ash.[7] These metals are human carcinogens and are categorized by the United States Environmental Protection Agency (U.S. EPA) as priority heavy metals because of their toxic effects on humans. As a result of open disposal, large quantities of heavy metals could enter water reserves, be it groundwater or surface water, and deteriorate the quality of the environment. Metal compounds change their phases rather than break down and can be transported by air or land to water through seepage and runoff from the sediment.[7] As Nei et al. detail, in Estonia, large quantities of cadmium, copper, zinc, lead, and other metals are present in oil shale waste; these metals enter soil and water compartments as ions.[8]

A secondary pollution exposure pathway may exist when working with or prolonged exposure to products like cement, which contain a significant fraction of spent fuel to increase the long-term stability of the cement. Heavy metals present in the oil shale ash and semicoke must be quantified to model the effects of exposure on those who use potential byproducts in concrete and other construction materials or spend prolonged time near disposal sites.[9,10] The ability to convert the semicoke waste to a useable byproduct, such as a sorbent material, could also be hindered by these heavy metals in a similar manner. The metals could either leach out of the semicoke during adsorption/absorption or possibly volatilize, causing harm to workers using the semicoke.

The disposal and/or byproduct conversion of oil shale semicoke may be detrimental to both the environment and human health because of entrained heavy metals. This study aims to determine levels of heavy metals present in oil shale and its semicoke in several samples from China and the United States to understand the obstacles that these metals pose to the widespread commercialization of energy from oil shale.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Five oil shale samples were investigated in this work. Two originated from the Maoming mine in the Guangdong province of southwest China, with the local Chinese classification (or grade) of A and C. One sample was obtained from the Huadian mine in the Jilin province of northeast China (grade C). Two samples were obtained from the Green River, Colorado (U.S.A.) deposits: one a high oil yield [50 gallons per ton (GPT)] sample and the other a lower oil yield (19 GPT) sample. All oil shale samples examined in this work were representatively sampled from larger scale mining exercises; each sample set investigated was further representatively sampled from 25 kg buckets. Each oil shale was ground and sieved in 100−200 g batches to yield samples with a particle size between 45 and 75 μm.

Approximately 5 g of each oil shale sample was pyrolyzed in a laboratory tube furnace maintained at either of two temperatures, 500

and 1000 °C, monitored with an Omega type K thermocouple directly above the sample accurate to ±0.5 K under a helium flow of approximately 300 cm^3 min^{-1} in a porcelain crucible. The mass loss from the pyrolysis procedure is attributed mostly to the removal of volatile matter (kerogen) and then, to a lesser extent, water removal and the decomposition of calcite and dolomite in the mineral portion of the shale. The Colorado 50 GPT and Chinese Maoming mine class A samples were also heated in an oxidative environment to yield 100% ash burnoff samples for testing to mimic the waste produced from firing or co-combusting oil shale and semicoke (because of sample size limitations, we could only perform the 100% burnoff for these two samples). Organic char contents and Brunauer−Emmett−Teller (BET) surface areas of samples pyrolyzed at 500 and 1000 °C are reported in previous work.[6]

2.2. X-ray Fluorescence (XRF) Measurements. A Thermo Fisher Scientific Niton Hand-held XL3t XRF analysis instrument was used to characterize the presence of metals. Because each element has a distinct set of energy levels, it emits X-rays at a unique set of energies. The set of energies allows the instrument to measure the elemental composition of a sample. XRF spectroscopy is rapid and does not damage or alter the sample, making it a preferred method for a variety of applications, such as metal and alloy analysis, mining and geochemical exploration, art and archeology, and quality control of consumer goods. Environmental applications specifically pertain to soil, dust, air filters, and drywall testing.[11]

We programmed the XRF to follow EPA method 6200 for "field portable XRF spectrometry for the determination of elemental concentrations in soil and sediment" for both *in situ* and *ex situ* soil samples.[12] This method was employed because it represents the closest in sample characteristics to the oil shale semicokes. The analytes measured in this method include the eight Resource Conservation and Recovery Act (RCRA) metals of arsenic, barium, cadmium, chromium, lead, selenium, and silver. The other elements measured using the XRF include molybdenum, strontium, zirconium, rubidium, throium, zinc, copper, iron, manganese, vanadium, titanium, scandium, potassium, sulfur, and calcium. The lowest detection limit of the XRF instrument is 9.2 mg/kg; for all of the oil shale samples, silver, cadmium, chromium, and selenium were below the lower detection limit (LOD) and are therefore not reported in the data tables.

Each time a sample is run in the XRF, the equipment takes three readings and tabulates the average parts per million (ppm) concentration of each metal along with 1 standard deviation. Each oil shale sample was measured 3 times to ensure reproducibility. The results discussed in this research are the average of the 3 runs (3 data points per run times 3 runs = 9 data points). The average of the three confidence intervals is reported as the overall confidence interval for each data set to preserve the magnitude of the margin of error. The results given in Table 1 are the concentration in ppm of metal in shale and respective confidence interval of 95% or ±2 standard deviations.

Each oil shale sample is loaded into a clean 31 mm diameter polyethylene sample cup with a clear window Mylar thin film (ThermoFischer gauge 0.000 24); the sample cup is filled approximately 1 cm high with oil shale/semicoke. The sample is lightly compacted with filter paper and cotton and sealed with a polyethylene cap. The sample was placed in the XRF stand and covered to absorb any excess X-rays. After the instrument was calibrated, the resolution was automatically set at 167.6 (keV) with an E scale of 7.4550. Prior to the sample runs, the "RCRA" soil sample standard, prepared in the same manner as the shale/semicoke samples, was used to standardize the instrument.

3. RESULTS AND DISCUSSION

XRF data are presented in Table 1 as ppm of each metal per oil shale sample with its 95% confidence interval. Our XRF results show heavy metal content similar to six Turkish oil shale samples

Table 1. XRF Data for Heavy Metal Concentrations in Oil Shale Samples in ppm with 95% Confidence Interval[a]

sample	arsenic	barium	calcium	copper	iron	potassium	manganese	molybdenum	lead
Colorado 50 GPT oil shale	67.9 ± 2.2	<LOD	106573 ± 5329	54.3 ± 6.6	15217 ± 173	17596 ± 80182.0	182.0 ± 64.2	29.2 ± 4.1	42.4 ± 7.8
Colorado 50 GPT 500 °C pyrolysis	79.4 ± 9.1	<LOD	95561 ± 4778	59.9 ± 19.1	19108 ± 377	14505 ± 725	293.5 ± 14.5	31.4 ± 2.1	45.8 ± 8.7
Colorado 50 GPT 1000 °C pyrolysis	104.3 ± 4.8	81.5 ± 2.0	98860 ± 4943	91.7 ± 22.7	25842 ± 647	15142 ± 757	353.7 ± 88.6	39.0 ± 2.6	<LOD
Colorado 50 GPT 100% burnoff	101.7 ± 9.1	176.6 ± 4.0	72453 ± 3623	93.0 ± 35.0	24585 ± 732	10092 ± 505	319.8 ± 90.6	38.3 ± 5.9	61.6 ± 10.6
Colorado 19 GPT oil shale	30.2 ± 4.3	219.8 ± 42.3	121425 ± 6071	32.9 ± 4.5	14925 ± 428	27413 ± 1371	282.9 ± 126	11.8 ± 3.4	27.7 ± 1.0
Colorado 19 GPT 500 °C pyrolysis	33.1 ± 6.3	118.2 ± 8.0	56534 ± 2827	41.3 ± 18.0	17673 ± 86	12923 ± 646	297.9 ± 59.0	14.6 ± 3.7	31.8 ± 4.3
Colorado 19 GPT 1000 °C pyrolysis	40.4 ± 4.5	338.6 ± 29.3	57460 ± 2873	44.7 ± 17.7	24471 ± 198	18528 ± 926	376.8 ± 33.2	18.5 ± 1.3	22.4 ± 2.6
Maoming A oil shale	22.3 ± 5.7	<LOD	27646 ± 1382	42.7 ± 12.5	32744 ± 732	3396 ± 170	678.3 ± 61.7	<LOD	18.4 ± 3.5
Maoming A 500 °C pyrolysis	28.0 ± 6.8	<LOD	22462 ± 1123	42.3 ± 20.1	39967 ± 884	3177 ± 159	795.6 ± 50.8	<LOD	25.6 ± 6.3
Maoming A 1000 °C pyrolysis	36.0 ± 6.3	275.4 ± 39.6	28427 ± 1421	53.3 ± 26.0	49391 ± 352	988.6 ± 179	988.6 ± 179	<LOD	<LOD
Maoming A 100% burnoff	41.6 ± 9.1	350.4 ± 68.4	22685 ± 1134	63.4 ± 14.0	53522 ± 991	3211 ± 161	1086.0 ± 148	<LOD	33.7 ± 8.3
Maoming C oil shale	30.7 ± 4.6	<LOD	14199 ± 710	32.0 ± 12.8	72761 ± 338	15662 ± 783	1085.8 ± 112	<LOD	33.1 ± 4.1
Maoming C 500 °C pyrolysis	41.2 ± 2.6	168.7 ± 10.5	6023 ± 301	<LOD	93338 ± 732	5822 ± 291	1527.4 ± 153	<LOD	47.8 ± 3.6
Maoming C 1000 °C pyrolysis	32.5 ± 5.8	227.5 ± 16.5	8205 ± 410	53.1 ± 28.6	100462 ± 732	8595 ± 430	1585.9 ± 74.6	<LOD	15.3 ± 5.8
Huadian oil shale	20.0 ± 8.1	<LOD	1051 ± 52.5	36.4 ± 3.5	28137 ± 403	8790 ± 440	139.9 ± 24.1	<LOD	39.6 ± 1.1
Huadian 500 °C pyrolysis	25.5 ± 5.9	<LOD	1207 ± 60.4	50.1 ± 27.4	37427 ± 152	10334 ± 517	204.7 ± 76.6	<LOD	55.0 ± 6.7
Huadian 1000 °C pyrolysis	24.3 ± 7.2	<LOD	1331 ± 66.5	61.0 ± 17.4	39359 ± 123	12680 ± 634	194.3 ± 51.4	<LOD	<LOD

sample	rubidium	sulfur	scandium	strontium	throium	titanium	vanadium	zinc	zirconium
Colorado 50 GPT oil shale	52.1 ± 4.3	159023 ± 7951	171.4 ± 27.5	532.1 ± 11.0	<LOD	1488 ± 90.2	145.8 ± 22.2	64.8 ± 3.3	58.0 ± 7.0
Colorado 50 GPT 500 °C pyrolysis	66.4 ± 5.1	117831 ± 5892	<LOD	664.5 ± 13.2	<LOD	1222 ± 96.0	120.6 ± 100.4	78.1 ± 17.3	66.6 ± 8.3
Colorado 50 GPT 1000 °C pyrolysis	81.8 ± 6.3	127531 ± 6377	<LOD	876.2 ± 16.7	14.2 ± 6.2	1344 ± 96.0	186.1 ± 6.3	<LOD	85.8 ± 10.3
Colorado 50 GPT 100% burnoff	80.9 ± 6.2	111522 ± 5576	<LOD	826.7 ± 16.1	13.0 ± 7.5	929.3 ± 96.0	155.7 ± 26.8	88.4 ± 11.3	82.9 ± 4.0
Colorado 19 GPT oil shale	59.3 ± 4.7	52368 ± 2618	150.4 ± 27.5	653.2 ± 5.8	<LOD	1766 ± 131	136.1 ± 22.5	50.2 ± 2.8	70.8 ± 5.9
Colorado 19 GPT 500 °C pyrolysis	66.3 ± 4.8	24363 ± 1218	115.1 ± 27.5	744.4 ± 6.5	<LOD	809.4 ± 127	<LOD	60.1 ± 7.1	75.8 ± 8.1
Colorado 19 GPT 1000 °C pyrolysis	90.0 ± 6.1	43210 ± 2161	220.6 ± 27.5	1000 ± 7.0	10.8 ± 6.8	1177 ± 96.0	95.8 ± 30.0	27.3 ± 9.9	104.2 ± 10.3
Maoming A oil shale	53.5 ± 4.3	102375 ± 5119	<LOD	423.0 ± 9.7	11.6 ± 5.0	1002 ± 96.0	<LOD	55.4 ± 11.4	119.7 ± 5.2
Maoming A 500 °C pyrolysis	66.8 ± 4.8	82539 ± 4127	<LOD	499.1 ± 6.6	12.9 ± 5.3	938.8 ± 96.0	<LOD	78.3 ± 9.8	133.2 ± 8.4
Maoming A 1000 °C pyrolysis	82.4 ± 5.7	145799 ± 7290	<LOD	602.8 ± 6.2	15.8 ± 5.9	1179 ± 96.0	58.3 ± 30.4	<LOD	164.3 ± 9.8
Maoming A 100% burnoff	81.2 ± 5.8	113500 ± 5675	<LOD	637.1 ± 8.9	15.8 ± 6.2	934.6 ± 96.0	<LOD	94.2 ± 16.9	183.7 ± 7.0
Maoming C oil shale	123.3 ± 6.2	148089 ± 7404	<LOD	189.6 ± 6.8	34.6 ± 6.7	2390 ± 96.0	<LOD	54.0 ± 8.6	111.1 ± 4.4
Maoming C 500 °C pyrolysis	161.9 ± 7.9	62148 ± 3107	<LOD	231.5 ± 8.4	50.7 ± 8.6	937.2 ± 96.0	<LOD	68.5 ± 16.9	125.3 ± 6.4
Maoming C 1000 °C pyrolysis	165.5 ± 8.2	85443 ± 4272	<LOD	257.6 ± 9.1	43.9 ± 8.4	1368 ± 73.8	<LOD	<LOD	142.9 ± 9.0
Huadian oil shale	151.5 ± 6.2	42789 ± 2139	<LOD	102.4 ± 3.5	45.0 ± 6.7	1755 ± 96.0	95.7 ± 1.9	80.5 ± 9.7	132.0 ± 2.2
Huadian 500 °C pyrolysis	192.0 ± 7.6	37403 ± 1870	<LOD	131.5 ± 5.7	55.6 ± 8.0	2029 ± 96.0	132.4 ± 12.9	103.7 ± 16.9	182.7 ± 4.6
Huadian 1000 °C pyrolysis	203.4 ± 7.8	38882 ± 1944	<LOD	139.7 ± 5.9	58.4 ± 8.0	1978 ± 96.0	141.4 ± 63.8	<LOD	170.2 ± 8.5

[a] <LOD indicates no detection/below detectable limit of 9.2 ppm.
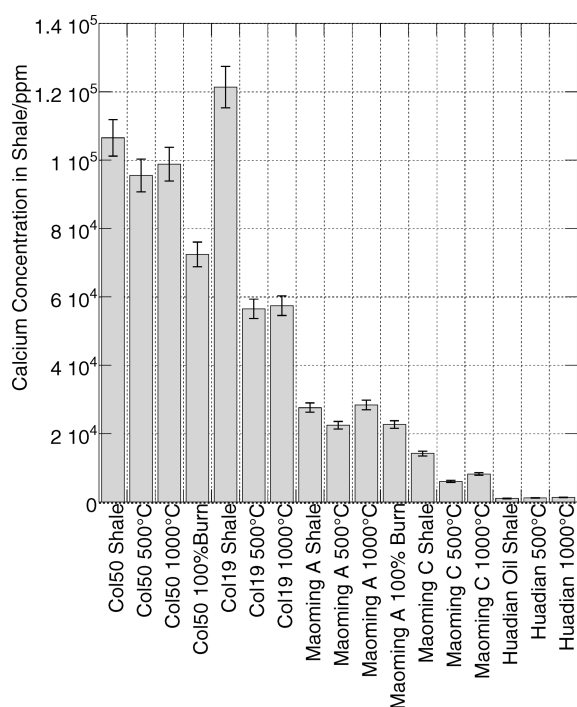
Figure 1. Calcium concentrations in all samples. Error bars indicate ± 2 standard deviations.
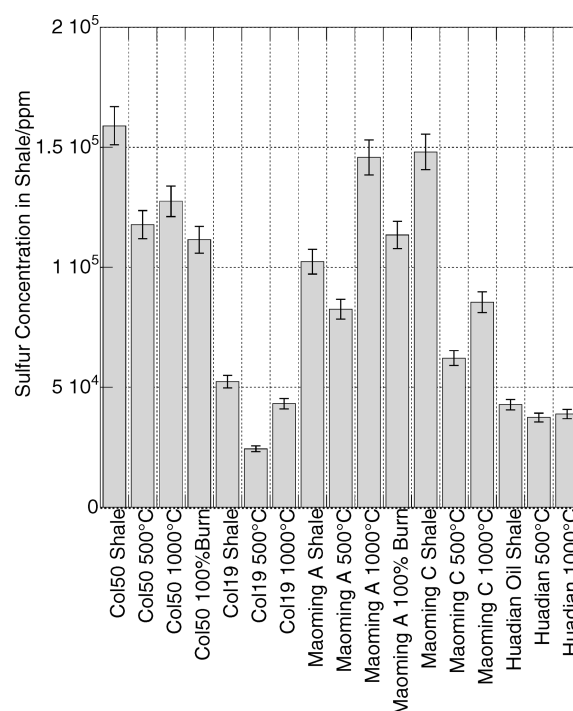

Figure 2. Sulfur concentrations in all samples. Error bars indicate ± 2 standard deviations.

analyzed by Kara-Gulbay and Korkmaz.[13] For example, Kara-Gulbay and Korkmaz find zinc levels in shales ranging from 0.10 to 95 ppm; we find LOD to 104 ppm. We find no detectable silver in our samples; they detect no more than 70 parts per billion (ppb) (below the LOD of the XRF).

Of the samples investigated herein, only the Colorado shales showed any detectable scandium and the Colorado 50 GPT pyrolyzed and 100% burnoff showed no Sc, whereas the 19GPT samples showed between 115 and 220 ppm in each sample. Scandium's average concentration in Earth's crust is 22 ppm, dispersed among other common rock-forming minerals.[14] Likewise, the Colorado shales were also the only samples with detectable molybdenum, commonly encountered in coal and coal fly ash. The Chinese shale samples were all higher in both rubidium and zirconium than the Colorado samples, and all sets of samples saw increasing rubidium and zirconium concentrations as the samples were progressively heat-treated (and volatile organics removed). Concentrations of thorium were also higher in the Chinese samples than in the Colorado samples and increased slightly with successive heat treatment, to be expected given it has the highest (known) melting point of all oxides in its most stable 4+ oxidative state, where it readily appears as ThO_2 and is responsible for most of Earth's internal heating.[15]

Raave et al. find that fresh oil shale semicoke is toxic to various plant seeds, although the toxic properties of semicoke decrease over time, attributed to weathering of the semicoke.[16] They remark that the cause of the phytotoxicity of oil shale semicoke to seeds is unknown, given the variable composition of inorganic and organic compounds of oil shale. However, Raave et al. note that it is doubtful that the phenols and polycyclic aromatic hydrocarbons present "cause the inhibition of seed germination", suggesting instead that "investigations published so far have paid no attention to the very high content of soluble inorganic compounds in the oil shale semi-coke". The authors suggest that

it is more likely the effect of high concentrations of calcium-, magnesium-, and sulfur-containing compounds that result in the inhibition of seed germination. Saether et al. note that the most common mineral ingredients (of import to agriculture) comprising oil shale ash are CaO, representing 30–44%, followed by SiO_2 (27–32%), K_2O (2.7–7.0%), and Fe_2O_3 (5.2–5.5%).[17] Indeed, we find relatively high values of calcium and sulfur present in all of our oil shale samples. Interestingly, the two Chinese class C shale samples (from Maoming and Huadian mines) have observed calcium and sulfur concentrations an order of magnitude lower than all other shale samples, as seen in Table 1 and Figures 1 and 2, respectively.

In Figure 1, we see that the concentration of calcium tends to decrease as it is heated, although the concentration differences between 500 and 1000 °C pyrolysis are fairly small. This is interesting, because between 250 and 600 °C most mass loss is attributed to the degradation of kerogen, whereas upward of this temperature range, mass loss is often attributed to decomposition of inorganic matter, such as calcite and dolomite. The remaining calcium is likely present in a non-elemental form that remains entrained in the semicoke upon heating. The two Colorado shale samples have significantly higher calcium content than the Chinese samples.

We see the opposite trend for arsenic concentrations. Figure 3 emphasizes the considerably higher concentration of arsenic present in the Colorado 50 GPT oil shale sample, as compared to the other four samples investigated. Because of the relatively low vapor pressure of solid arsenic, 0.081 atm at 504 °C, and high enthalpy of sublimation, 154.7 kJ mol^{-1} at 504 °C, arsenic will tend to remain in the solid phase as opposed to volatilizing.[18] Because arsenic frequently forms inorganic complexes with oxygen, chlorine, and sulfur in the environment, we suspect (given the high levels of sulfur present) that a portion of the arsenic detected is contained in an inorganic compound as opposed to the elemental
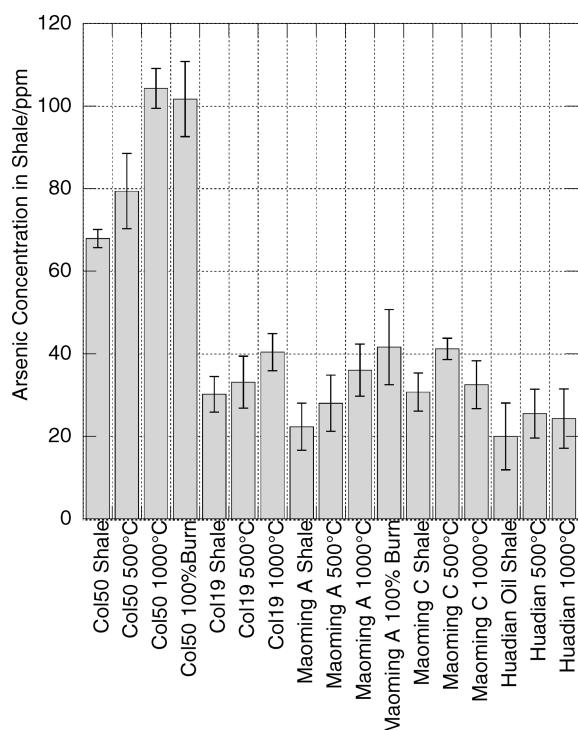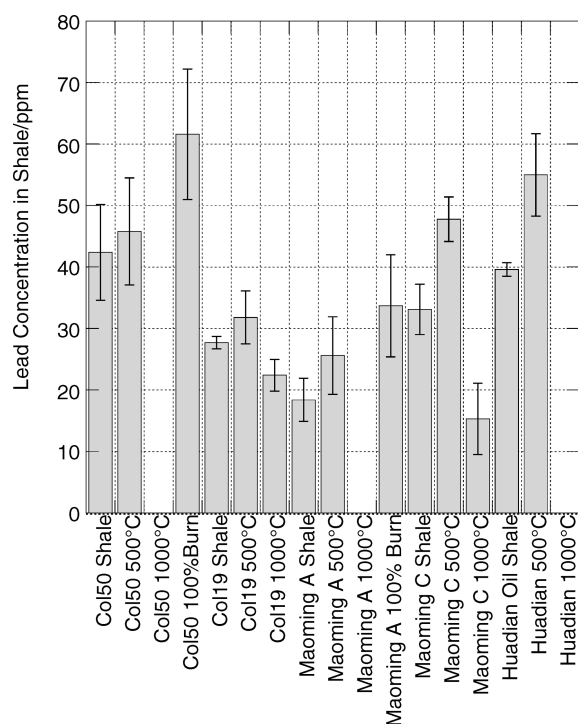
Figure 3. Arsenic concentrations in all samples. The error bars indicate ±2 standard deviations.

Figure 4. Lead concentrations in all samples. Error bars indicate ±2 standard deviations.

form but cannot conclude anything based on quantities of such compounds with the XRF data alone. The slight increases in the concentration of arsenic as organic matter is lost from oil shale to 500−1000 °C pyrolysis suggests that, while some of the arsenic may leave the vapor phase, the majority remains in the shale materials.

Arsenic is naturally found in rocks and soils, and its concentration is dependent upon the geology of the region and past anthropogenic inputs. We often see elevated concentrations with igneous and sedimentary rocks, especially those with sulfidic ores.[19] The U.S. EPA's ecological soil screening level (Eco-SSL) for plants for arsenic is 18 ppm (18 mg of arsenic/kg of soil loading), and for the protection of mammaliam wildlife, the Eco-SSL is 46 ppm. Eco-SSLs are concentrations of contaminants in soil protective of ecological receptors that commonly contact and/or consume biota that live in or on soil to protect terrestrial ecosystems.[20] The arsenic concentrations in the oil shale samples ranged from a low of 20 ppm (Huadian oil shale) to 104 ppm (Colorado 50 GPT 1000 °C pyrolyzed); all of the Colorado 50 GPT samples were above the 46 ppm Eco-SSL, while the other four shale and semicoke samples were all below 46 ppm. Dependent upon natural arsenic levels in surrounding soils, the oil shale semicoke should only have a moderate effect on increasing arsenic levels in the surrounding area, likely below the Eco-SSL, after incorporation with surrounding soils. However, without dilution, the arsenic level is significantly above EPA's 2010 regional screening level (RSL) for chemical contaminants at superfund sites (regions 3, 6, and 9 compiled) of 0.39 and 1.6 ppm for residential and industrial soil, respectively.[21]

The concentrations of both lead and copper present in all five samples are orders of magnitude lower than the arsenic, calcium, and other metals present, as shown in Figures 4 (lead) and 5 (copper). Here, we find that lead is significantly below the EPA

RSL of 400 and 800 ppm for residential and industrial soil, respectively. In addition, Adamson et al. note that concentrations of lead leached from oil shale ash mixtures are negligible.[22] Likewise, the copper present in all oil shale semicokes is below the EPA RSL of 3100 and 4100 ppm for residential and industrial soil, respectively, suggesting that the oil shale samples do not pose a threat at these concentrations if the semicoke is landfilled. While there was a detectable amount of strontium in every sample (ranging from 102 to 1000 ppm), this is significantly below the EPA RSL of 47 000 ppm for residential soil.

Barium was detected in half of the samples studied at concentrations ranging from 82 to 350 ppm; the Huadian oil shale samples had no detectable barium, whereas the Colorado 19 GPT samples had detectable barium in each sample. The EPA RSL for barium in residential soil is 15 000 ppm. For the Colorado 50 GPT and Maoming A and C samples, barium present in the oil shale sample was below the lower limit of the detector. However, after pyrolysis at 500 °C, we detected 169 ppm of Ba in the Maoming C sample, although not in the other two. After 1000 °C pyrolysis, 82, 276, and 228 ppm of barium in the Colorado 50, Maoming A, and Maoming C samples, respectively, were detected. With each heat treatment, the carbon content decreases. This suggests that essentially all of the barium present initially remains in the semicoke because it was originally below the lower detection limit; if the barium was volatilized and carried along in the He carrier stream in an amount approaching its original concentration with the carbon, it would remain undetected in subsequent samples. One potential anomaly that we note is the Colorado 19 GPT oil shale sample. Barium was originally detected at a concentration of 220 ppm (using three separate samples); for the 500 °C pyrolyzed sample, it dropped to 118 ppm; and it went back to 339 ppm for the 1000 °C pyrolysis.
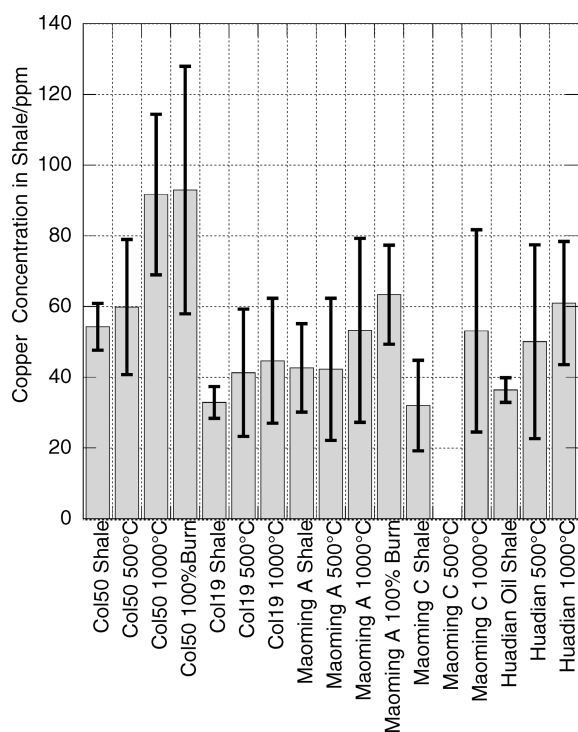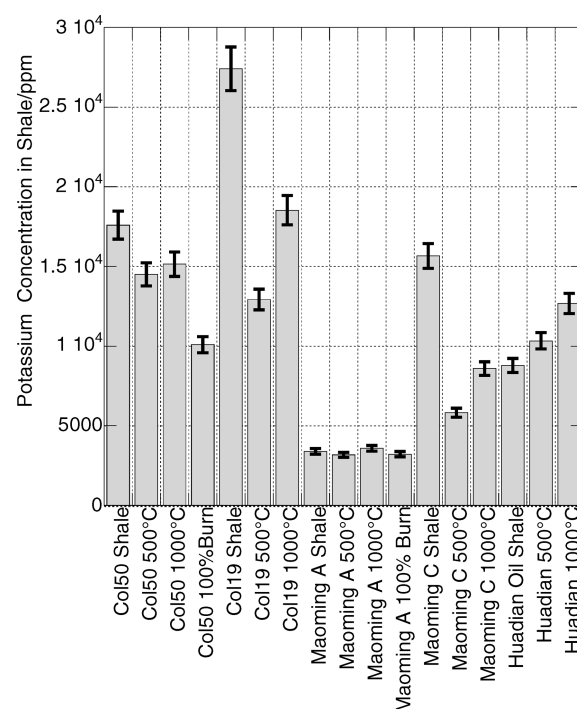
Figure 5. Copper concentrations in all samples. Error bars indicate ±2 standard deviations.

Figure 6. Potassium concentrations in all samples. Error bars indicate ±2 standard deviations.

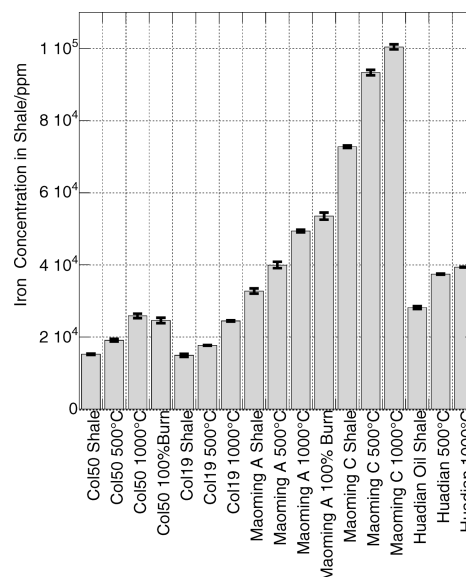**Figure 7.** Iron concentrations in all samples. Error bars indicate ±2 standard deviations.

Although we ran this measurement with several portions of the 5 g pyrolyzed sample, we obtained the same result.

We find this same trend for potassium in the Colorado 19 GPT samples, as seen in Figure 6. Potassium decreases from 27 413 to 12 923 ppm and then back to 18 528 ppm for the oil shale, 500 °C pyrolysis, and 1000 °C pyrolysis, respectively (we note that, although there is a slight increase in potassium from 500 to 1000 °C pyrolyzed for 50 GPT, this could well be within the margin of error). The Maoming mine class A samples all have roughly similar concentrations of potassium present, whereas the Maoming class C sample decreases for 500 °C pyrolysis and then increases for 1000 °C pyrolysis. Reasons for such anomalies would likely center around the chemical form of potassium (and barium) assumed. Given differences in vapor pressures, chemical affinities, and other thermodynamic properties for compounds comprised of various anions with K and Ba, some compounds may be more likely to be volatilized at lower temperatures than others. Saether et al. note that, between 2.7 and 7.0%, oil shale ash is often comprised of K_2O,[17] which concurs with the large variations in potassium detected in our samples.

Figure 7 presents the concentrations of iron in each sample; here, we see that the concentration of iron increases for each successive heat treatment for every shale sample, indicating that a majority of iron is likely bound in inorganic compounds that have lower vapor pressures and higher enthalpies of vaporization to keep it entrained in the semicoke. The iron present in each sample (with the exception of the Maoming mine class A 1000 °C pyrolyzed and 100% burnoff and all Maoming mine C samples) is below the EPA RSL of 55 000 ppm for residential soil. Likewise, the vanadium present in all samples is well below the EPA RSL of 390 ppm for residential soil for vanadium compounds. However, the EPA RSL for metallic vanadium is 5.5 ppm, which suggests that further research is needed into whether or not this metal is

present in its elemental form or as a compound, to ensure that open landfilling is an appropriate mechanism of disposal with respect to vanadium.

The EPA RSL for metallic zinc in residential soil is 23 000 ppm; while we do not know the compound and oxidation state that zinc present assumes, the highest detected concentration of zinc across the samples was 103 ppm for the Huadian 500 °C pyrolyzed sample. Interestingly, the unpyrolyzed Huadian shale has approximately 81 ppm of zinc, whereas none was detected for the 1000 °C pyrolyzed sample. The vapor pressure of zinc oxide,
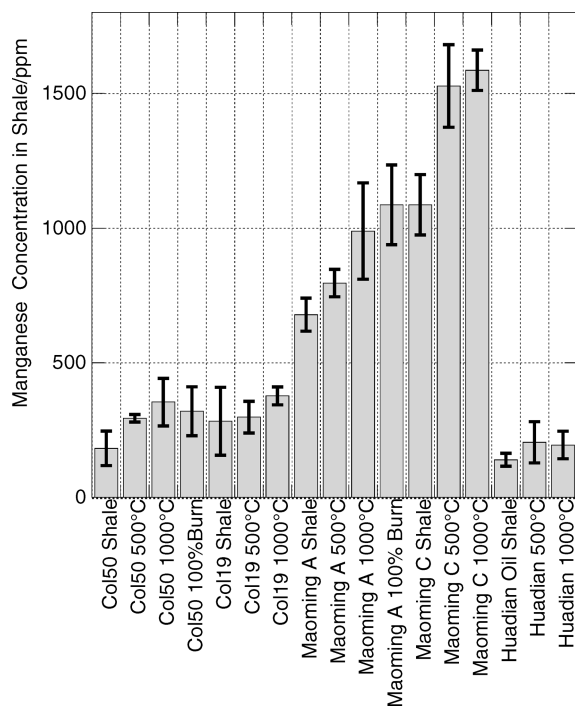
Figure 8. Manganese concentrations in all samples. Error bars indicate ±2 standard deviations.

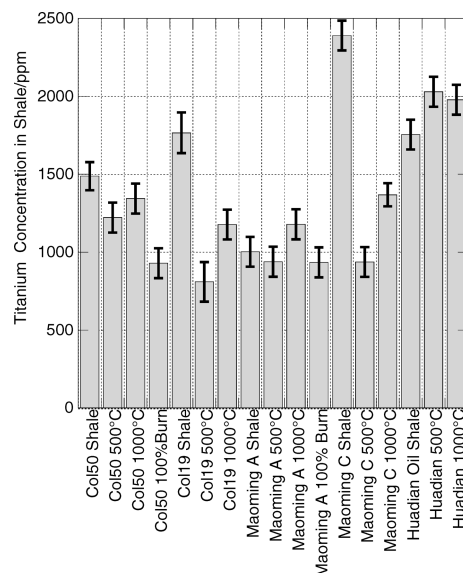**Figure 9.** Titanium concentrations in all samples. Error bars indicate ±2 standard deviations.

a plausible form for the zinc to assume, is quite high, upward of 4 Pa at 1000 °C.[23] Conversely, the vapor pressure of zinc sulfide is approximately 0.001 Pa at the same temperature,[24] demonstrating a lower capacity to volatilize from the oil shale sample.

Figure 8 details the concentrations of manganese in each sample. We see that the Colorado 50 and 19 GPT samples as well as the Huadian mine samples are all less than 500 ppm, well below the EPA RSL for (non-diet) manganese of 1800 ppm in residential soil. The Maoming mine class A and C samples are also below this recommended soil threshold, although here we see higher levels of manganese in the heat-treated shales than the original shale samples, with levels climbing upward of 1500 ppm.

Finally, in Figure 9, we see the relatively stable concentrations of titanium across all shale samples. The Maoming class C untreated shale sample has the highest concentration of Ti, measured at 2390 ppm, which is cut in half upon pyrolyzing at 500 °C. Conservation of mass principles dictates that, if we are losing carbon (Maoming class C shale ∼30% organic content to 17% char at 500 °C pyrolysis) and the Ti concentration also decreases, some of the titanium must also be lost during pyrolysis.[6,25]

In analyzing shale samples from the Huadian mine, Yan et al. find strong variations in reactivity of co-pyrolyzed (shale and semicoke) samples between 600 and 800 °C, attributing this to a possible encapsulation of undecomposed minerals and organic matter.[25] As such, minerals in samples with less inorganic matter were more readily decomposed than those with higher inorganic matter at the same temperature. This finding directly relates to our result; if one potential byproduct pathway is co-combustion or co-pyrolysis of oil shale semicoke, the inorganic content will significantly impact reactivities and therefore process efficiencies.

Sun et al. demonstrate that total concentrations of heavy metals in soil, especially lead and zinc, decrease with an increasing distance from the source, in this case, mine tailings. They attribute this to differences in leaching, translocation, and

accumulation of different metals released from the tailings into the soil.[26] In a study to assess the reliability of earthworm uptake of heavy metals from oil shale waste as a bioindicator, Nei et al. conclude that the content of heavy metals in earthworm populations decreased over time in an area where oil shale combustion was phased out,[8] seconding the data by Sun et al.

While the heavy metal content of many of the semicoke samples are considerably below EPA RSL values, the ability to employ semicoke as an *in situ* environmental sorbent is questionable. Further studies should be undertaken to determine if the heavy metals present in the semicoke leach out during sorption operations, essentially replacing one contaminant with another, although leaching studies from semicoke piles, such as those mentioned herein, are a reasonable gauge of such transport. Such information would also assist in determining the true environmental impact of common open-air disposal of semicoke, answering the questions as to whether or not the heavy metals remain within the semicoke or leach into groundwater and at what rate this occurs. However, the data provided herein can be used as a "worst-case" scenario estimate for environmental contaminant loading.

4. CONCLUSION

While the transport and bioavailability of heavy metals present in oil shale semicoke and ash are highly dependent upon the type of soil, semicoke/ash, leaching conditions, prevailing atmospheric conditions, and a variety of other factors, the concentrations of heavy metals measured here lead to several baseline observations on the impact of these metals on the environment and human health. In terms of open disposal of oil shale semicoke, the arsenic levels detected in some of the shale samples are potentially problematic in terms of leaching into groundwater and aerosolizing. Overall, the Colorado 50 GPT shale samples had the highest arsenic concentrations of the shales investigated herein. Arsenic concentrations increase slightly as organic matter is lost from oil shale to 500 to 1000 °C pyrolysis, suggesting that a small fraction of arsenic may be lost from the semicoke in the vapor phase upon heating but that the majority remains in the shale material. In terms of byproduct conversion, these elevated

arsenic levels could mitigate the potential benefits of an environmental sorbent byproduct conversion, unless they remain bound to the semicoke (plausible given the high specific surface areas and reactivities of the semicokes) or are removed in a pretreatment step.

As expected, shale origin appears to dictate the concentrations of some heavy metals present in the initial oil shale. For example, the three Chinese oil shales have significantly higher iron, thorium, and zirconium concentrations than the two Colorado shales. The Colorado shales have higher calcium contents than the Chinese shales. Conversely, the Maoming C and Huadian mine shales have concentrations of rubidium twice as high as the Maoming A and two Colorado shales.

The other heavy metals detected in oil shale semicoke using XRF are below U.S. EPA RSLs for superfund sites and do not appear to represent a significant problem to the environment with open air disposal of oil shale semicoke. On the other hand, the ability to use the semicoke as a byproduct (i.e., as a sorbent or as an additive in concrete) may be hindered slightly depending upon the application at hand by the heavy metals detected in this study.

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