**Trace Metals Accumulation in a Coal-fired Post Combustion CO₂ Capture Process with
Amine-based Solvents**

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19 **Abstract**

20 Trace elements contained in coal-derived flue gas can accumulate in solvents used in post-
21 combustion CO₂ capture with potential process and environmental impacts. The accumulation of
22 six metals, arsenic, mercury, selenium, iron, nickel, and copper in three amine-based solvents
23 was investigated in a 0.1 MWth post-combustion CO₂ capture pilot unit from the combustion of
24 coal for testing periods of 200 – 400 hours. Generally, the concentration of the metals increased
25 over time at varying rates, with the coal used being the principal source for the build-up of most
26 of them. The relatively lower concentrations of iron, nickel, and copper in one of the solvents
27 showed that the type of solvent influenced its interaction with the metals and the rate of metals
28 accumulation.

29 **Keywords:** CO₂ capture, trace elements, heavy metals, flue gas, amine solvents
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Introduction

Regulations to mitigate the environmental impacts of greenhouse gases such as CO₂ continue to drive the quest for viable processes for CO₂ capture. The U.S. Department of Energy (DOE) has set a cost goal of ≤\$40/tonne for 90% CO₂ removal to be achieved in the 2020–2025 timeframe for technologies to be ready for deployment (NETL-DOE, 2014). Among the various capture technologies being pursued, post-combustion CO₂ capture using chemical absorption is considered one of the most promising and is particularly suitable for new and retrofitting existing coal-fired power plants as no major modifications in the combustion process would be required. Amines have been extensively studied and continue to be explored as solvent candidates of choice for the process (Puxty et al., 2009; Rochelle, 2009). As this method for CO₂ removal continues to be developed, progressing from the lab scale to the commercial scale, it is important to understand the broad environmental impacts that it will have relating to spent solvent disposal, degradation rates and products, secondary emissions, and the interaction and accumulation of coal constituents in the solvent.

Apart from CO₂, coal combustion results in emissions defined by the US EPA, such as SO_x, NO_x, particulate matter, and trace elements such as copper, iron, mercury, nickel, zinc, vanadium, chromium, lead, arsenic, cadmium, etc. depending on the coal composition (Cordoba et al., 2012; Saarnio et al., 2014). Control techniques such as low NO_x burners (for NO_x reduction), flue gas desulfurization (for SO_x reduction), electrostatic precipitators and bag house filters (for particulate matter removal), and carbon injection (for mercury removal) are employed to reduce the environmental impacts and associated health risks of these emissions (Saarnio et al., 2014). For coal-fired power plants the coal quality and types of control techniques used affect the type of emissions. During combustion, pollutants partition into various emission streams such as bottom ash, fly ash, and flue gas. A major portion of almost all trace elements, particularly metals, are bound in the fly ash where they can be concentrated and the highly volatile elements, like mercury, are carried with the flue gas (Xu et al., 2003; Cotton et al., 2014). For post-combustion CO₂ capture, where the flue gas is further treated by direct contact with a solvent for CO₂ removal, the fate of the trace elements carried over with the flue gas and in the entrained fly are of paramount interest. As noted, when residual ash is captured by the solvent, there is a potential for the release of significant amounts of iron, magnesium and calcium, for example, which have varied effects in promoting the degradation of the solvent (Schallert et al., 2013). It has been shown in laboratory (Sexton and Rochelle, 2009) and pilot scale studies (Mertens et al., 2013) that the presence of metal ions like iron can catalyze the oxidative degradation of monoethanolamine (MEA) and it is therefore imperative to control accumulation to reduce degradation emissions, such as ammonia, in the process.

Many studies have been carried out to understand solvent degradation pathways and the environmental impacts of the resulting degradation products from the capture process (Strazisar et al., 2003; Davis and Rochelle, 2009; Lepaumier et al., 2009, 2011; Zhou et al., 2012; Huang et al., 2014). The recent focus of these studies on the atmospheric release of amines and amine degradation products and the knowledge gained have allayed concerns about the uncertainty of potential health and environmental risks posed by the capture process (Gjernes et al., 2013). While some work has been done on the impacts of flue gas contaminants such as acidic impurities on solvent degradation, the potential impacts of other contaminants such as trace metallic elements has not been considered in much detail. The growing concern about the health effects of exposure to heavy metals requires an understanding of the levels of accumulation, process impacts, and potential mitigation strategies to deal with any adverse effects they may present.

This work explores the build-up of several metallic elements over time in amine-based solvents in a 0.1 MWth coal fired post-combustion chemical absorption pilot scale CO₂ capture process. Many metals are known to have specific environmental effects and eight are regulated by the Resource Conservation and Recovery Act, (RCRA) of 1976, including arsenic, mercury, and selenium, which are studied in this work. The other elements examined are iron, nickel, and copper.

Experimental

Process and Operation

The experiments were carried out for three different amine-based solvent blends (Solvents A, B, and C) in which the accumulation of six metals (As, Hg, Se, Fe, Ni, and Cu) were monitored for periods of 200 to 400 run hours for each campaign in the UKy-CAER 0.1 MWth-scale coal-fired post-combustion CO₂ capture pilot unit shown in Figure 1. The primary purpose of this unit, constructed in 2007, is for solvent performance evaluation. Based on these evaluations, specifically the associated energy penalty, the solvent may, or may not be selected for longer-term studies. Given this purpose, it is more common that solvents are evaluated for a relatively

short amount of time, hundreds of hours. Flue gas was generated by combusting Pennsylvania sub-bituminous coal with air in a 200,000 BTU/hr combustion unit shown in Figure 2.

Figure 1. Pilot unit for CO₂ capture.

Figure 2. Coal combustion unit for flue gas generation and SO₂ scrubbing unit.

A schematic diagram of the CO₂ capture process is shown in Figure 3. Flue gas from the combustion chamber first passes through a solids separator where particulates are removed. The gas is then cooled and treated with a wet desulfurization process to lower the SO₂ concentration. An induced draft fan sends the flue gas to a knockout drum where additional particulates and condensate are removed. At this point, the CO₂ concentration in the flue gas is 8 – 11 vol%, and this is boosted to ~14 vol% with compressed CO₂ gas before the flue gas is sent to the bottom of the packed absorber. The CO₂ doping allows for consistent experimental conditions, while still reflecting a true commercial scenario with respect to other coal impurities. The absorber and stripper are described in detail elsewhere (Frimpong et al., 2013) and their characteristics and typical operating conditions for the experiments are summarized in Table 1. After CO₂ in the flue gas is absorbed in the solvent, the rich solvent exiting the absorber is pumped through the rich/lean cross-heat exchanger into the stripper where the solvent is regenerated. This process is operated at a higher stripping pressure than typical to deliberately promote solvent degradation for research purposes. The lean solvent is then pumped back to the top of the absorber via the cross-heat exchanger and the polishing chiller, which conditions the solvent to the desired inlet temperature. Due to the typically corrosive nature of amines, the primary materials of construction of this process are 304SS and 316SS.

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Table 1. Unit specifications and typical operating conditions

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Analysis

The accumulation of metals (As, Hg, Se, Fe, Ni, and Cu) in three different amine-based solvent blends were determined by analyzing periodic liquid samples drawn approximately every 20 hours from the process using inductively coupled plasma mass spectrometry (ICP-MS) during the course of the campaigns which varied between 200 – 400 hours. The instrument used was a Thermo Electronic Inc. Xseries (II). Samples were prepared with a microwave assisted digestion system with a dilution factor of 1 to 10. For Hg, the calibration range was 0.1 ppb – 50 ppb, with a method detection limit of 0.1 ppb. For all other elements the calibration range was 5 ppb – 1000 ppb, with a method detection limit of 1 ppb. The calibrations were performed with the solvents, nanopure water, and a similar dilution factor. Each measurement was repeated three times. Relative standard deviation values were generally <5%, with an accuracy of 10%. The Pennsylvania bituminous coal used for the experiments was initially characterized to provide a reference for the constituent amounts of the elements present in the coal. The mercury content was measured directly via atomic absorption spectrophotometry with a detection limit of 10 ppb and a repeatability of 5 ppb for two measurements. The selenium content of the coal was determined by ICP after digestion with a detection limit of 0.1 ppm and a repeatability of 0.05 ppm for two measurements. Other analyses performed on the coal included proximate, ultimate and ash content. The instruments and analyses performed are summarized in Table 2.

Table 2. Coal analyses performed and instruments used.

Test	Instrument (Model)	Determination
Proximate analysis	Leco TGA-601	Moisture, ash, volatile matter, fixed carbon contents
Ultimate analysis	Leco CHN-628	Carbon, hydrogen, nitrogen, sulfur, ash contents
Ash	PANalytical PW2404	26 major and minor constituents
Mercury content	Leco AMA254	
Selenium content	Varian 720-ES ICP-OES	

Results and Discussion

The results for the proximate, ultimate, ash, mercury, and selenium analyses for the Pennsylvania coal used are shown in Tables 3, 4, and 5, respectively.

Table 3. Proximate and ultimate analyses of coal.

Component	Amount (%)
<i>Proximate</i>	
Moisture	1.1

Volatile matter	19.7
Fixed carbon	77.2
Carbon	67.0
Ultimate	
Carbon	77.2
Hydrogen	4.3
Nitrogen	1.2
Oxygen	4.1
Sulfur	1.1
Ash	12.2

Table 4. Ash analysis of coal.

Minor Compounds		Trace Elements			
Component	Amount (%)	Component	Amount (ppm)	Component	Amount (ppm)
SiO ₂	38.2	V	2875	Pb	46
Al ₂ O ₃	25.9	Sr	1993	Mo	10
Fe ₂ O ₃	17.8	Ba	1462	Sb	6
TiO ₂	12.9	Cl	269	Cd	1
CaO	1.2	Mn	246	Rb	<1
MgO	0.95	Ni	111	Zr	<1
P ₂ O ₅	0.49	Cu	99		
SO ₃	0.35	Zn	99		
K ₂ O	0.12	As	92		
Na ₂ O	0.01	Co	64		

Table 5. Mercury and selenium analyses of coal.

Component	Amount
Mercury	96 ppb
Selenium	4 ppm

Figures 4 – 9 show the metal concentration as a function of time for the three solvents, including one primary amine, one secondary amine, and one blended amine solution. It should be noted that no data was excluded in these graphs. Even though there are a few outlying points, general trends are evident.

As shown in Figure 4, the levels of selenium did increase over time with a similar rate for all three solvents evaluated. In each case, levels grew by an order of magnitude by 200 run hours from a level of hundreds to thousands of parts per billion. The level continued to rise by another three times from 200 to 400 run hours in Solvent C to a level of 6000 ppb. As selenium is not a corrosion product of stainless steel and was detected in the coal, it is reasonable to assume that the source of selenium is carry over ash or flue gas from the coal combustion.

Figure 4. Selenium concentration accumulation in three amine solvents used for post-combustion CO₂ capture.

As with selenium, levels of arsenic also increased over time with a similar rate for all three solvents evaluated, as shown in Figure 5. In each case, initial levels were approximately 10 ppb and increased at least three times to between 30 and 50 ppb after approximately 200 run hours. In the case of Solvent C, the arsenic level increased another two times to a level of 60 ppm from 200 to 400 run hours. The ash analysis results performed on the coal does show arsenic content and it is reasonable to assume that carry over combustion fly ash is the source of the arsenic. There are two outlying points that cannot be explained for Solvent C, at approximate run hours 50 and 60, where the arsenic levels jumped up to 67.9 and 66.9 ppb, respectively. There is nothing operationally, that would explain this sharp increase and an increase of other metals at the same run interval is not observed. Neither is there any reason to discount the validity of these points, as the samples were prepared and analyzed following the same procedure as all the others.

Figure 5. Arsenic concentration accumulation in three amine solvents used for post-combustion CO₂ capture.

Interestingly, the levels of mercury were not observed to increase, as shown in Figure 6. In the cases of Solvents B and C, levels remained below the instrument detection limit for the duration of the test. Levels of mercury were detected in Solvent A, but an accumulation trend cannot be established. Mercury is also not a component of stainless steel, so if mercury were observed to increase, the source would be the coal.

Figure 6. Mercury concentration accumulation in three amine solvents used for post-combustion CO₂ capture.

As shown in Figure 7, copper levels increased in the case of all three solvents evaluated. In the case of Solvent A, copper levels started at 14 ppb and rose by 68 times to a level of 955 ppb. The copper content actually remained fairly constant until about 100 run hours, when the levels rapidly increased. The copper level trend is not as clear in the case of Solvent B. Copper levels were found to be both above and below an average of about 40 ppb until about 170 run hours, when the level increased significantly. In the case of Solvent C, a steady increase was observed from an initial level of 7 ppb by nearly 6 times to a level of 40 ppb. Copper is not a constituent of stainless steel, and it is present in the coal ash at about 100 ppm, as shown in the ash analysis. It is reasonable to conclude that the source of the copper is the coal itself.

Figure 7. Copper concentration accumulation in three amine solvents used for post-combustion CO₂ capture.

As shown in Figure 8, levels of iron also increased over time for all three solvents. Initial levels were 1712 ppb, 1446 ppb, and 138 ppb for Solvents A, B, and C, respectively. In the case of Solvents A, iron levels rose 3.6 times to 6207 ppb after 200 run hours. In the case of Solvent B, iron levels rose 1.9 times to a level of 2826 ppb after 200 run hours. In the case of Solvent C, iron levels rose 2.8 times to a level of 400 ppb after approximately 200 run hours, and 11.9 times to a level of 1651 ppb after 400 run hours. At 103 and 106 run hours the iron level in Solvent A was observed to spike to 25,500 and 26,700 ppb, respectively. The iron levels then fall off again, and unfortunately the solvent campaign reached an end before the details of the trend could be established, but at the very least, it is safe to say the iron levels did, indeed, increase over time.

There might be several sources of the iron observed to accumulate in the solvent. First, iron in the solvent may be a consequence of corrosion as it is the largest component of the stainless steel (as much as 70%) used in the process piping and vessels. Second, iron may be from the coal ash, as ferric oxide (Fe₂O₃) is a significant component, as shown by the ash analysis. Finally, iron may well exist in make-up water added to the system, although this water quality has not been analyzed.

Figure 8. Iron concentration accumulation in three amine solvents used for post-combustion CO₂ capture.

As shown in Figure 9, nickel concentrations also increased over the run time for all three solvents evaluated. In the case of Solvent A, the nickel level started at 41 ppb and rose by more than 100 times to 4597 ppb after 200 run hours. In the case of Solvent B, the nickel level started at 505 ppb and rose by 6 times to 3210 ppb after 200 run hours. In the case of Solvent C, the nickel level started at 99 ppb and fell to a low value of 36 ppb after approximately 200 run hours. The trend then reversed and nickel levels rose to 161 ppb.

Nickel is a significant component of stainless steel (10 -15%), so the source of the nickel could be a corrosion product. An additional source of nickel is the coal, as nickel is present in the coal ash at a level of 100 ppm, as shown by the ash analysis.

236

237 Figure 9. Nickel concentration accumulation in three amine solvents used for post-combustion
 238 CO₂ capture.

239 The metals considered in this study represent metals that might accumulate from three sources:
 240 the coal itself, the make-up water, or the corrosion of the process materials of construction.
 241 Certainly this is not comprehensive and other metals may also be present. There are many
 242 unknowns. The variations of metal concentrations may be attributed to solubility differences in
 243 the different solvents, variations of coal composition, or variations of flue gas generator
 244 combustion conditions, which could affect the amount of fly ash in the solvent.

245 When evaluating amine Solvent A for a duration of 200 run-hours, levels of iron, nickel, copper,
 246 arsenic and selenium were all observed to increase. Mercury levels were not observed to
 247 increase, even though it was present in the uncombusted coal at 100 ppm. Arsenic and nickel
 248 showed clear, steady increases over the observation time. Iron levels were more varied, but a
 249 general increase is still observed. The greatest percent increase was observed for nickel from 50
 250 to 4600 ppb. Arsenic levels rose from 10 to 50 ppb, and was present in the coal ash at about 100
 251 ppm. Nickel contributions could come from the coal and/or as a corrosion product of stainless
 252 steel. Nickel was present in the coal ash at about 100 ppm and is a significant constituent (10 –

15%) of stainless steel. Iron levels rose from 2000 to 6000 ppb. Iron contributions could come from the coal and/or as a corrosion product of stainless steel. Ferric oxide (Fe_2O_3) was present in the coal ash at about 18% and is the primary constituent (about 70%) of stainless steel. Copper levels rose from 10 to 1000 ppb, and was present in the coal ash at about 100 ppm. Selenium levels rose from 170 to 1100 ppb, and was present in the uncombusted coal at about 5 ppm.

These results were duplicated in an evaluation with amine Solvent B for a duration 200 run-hours. Again, levels of iron, nickel, copper, arsenic, and selenium were all observed to increase, while mercury levels were not observed to increase. Nickel, iron, selenium and arsenic levels showed steady increase over time while the copper levels were more varied. The greatest percent increase was observed for selenium from 140 to 2000 ppb.

Finally, similar results were observed with amine Solvent C. For a third time, levels of iron, nickel, copper, arsenic, and selenium were observed to clearly and steadily increase over a duration of 400 run-hours. Mercury levels were for a third time not observed to increase. Selenium levels were observed to increase by the greatest amount from 340 to 6040 ppb, followed closely by the increase in iron levels from 130 to 1700 ppb. Copper levels rose from 7 to 71 ppb. Arsenic levels rose from 14 to 60 ppb. Nickel levels rose from 100 to 160 ppb.

Iron and nickel are constituents of stainless steel, which is commonly used with amine process fluids and is used in this process. In the case of solvent A, based on corrosion rates found in the literature, it is possible that the levels of iron and nickel accumulation are completely related to corrosion of stainless steel material of process construction [Cousins et al., 2014]. It is clear that the corrosion process is measurably lessened in the case of solvent B and significantly lessened in the case of solvent C.

Tabular representation of all data points are given in Tables 6 – 8.

Table 6. Metal concentration values measured in Solvent A.

Approximate Cumulative Run Hours	Se (ppb)	As (ppb)	Hg (ppb)	Cu (ppb)	Fe (ppb)	Ni (ppb)
10	174.9	13.04	0.145	14.45	1712	41.3
40	412.5	22.83	0.117	19.36	1799	65.9
80	781.9	37.38	0.077	13.46	3971	125.2
100	738.2	39.57	0.165	10.24	25573	638.7
110	983.0	43.29	0.201	18.49	23695	4346
150	982.3	49.46	0.154	483.9	8158	5212
160	1100	51.01	0.141	1064	7973	4953
190	1096	48.35	0.132	955.2	6207	4597

Table 7. Metal concentration values measured in Solvent B.

Approximate Cumulative Run Hours	Se (ppb)	As (ppb)	Hg (ppb)	Cu (ppb)	Fe (ppb)	Ni (ppb)
20	137.6	9.03	0.0	26.51	1446	505.1
30	380.5	16.39	0.0	1.112	1442	3051
70	738.6	23.24	0.0	21.52	2426	3183
80	948.8	31.65	0.0	147.6	3091	3289
100	956.9	33.55	0.0	46.88	2741	2959
120	886.3	33.28	0.0	17.61	1917	2967
160	1524	39.59	0.0	6.633	2270	3175
180	1706	39.22	0.0	69.21	2608	3137
190	1960	40.01	0.0	102.2	2826	3210

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280 Table 8. Metal concentration values measured in Solvent C.

Approximate Cumulative Run Hours	Se (ppb)	As (ppb)	Hg (ppb)	Cu (ppb)	Fe (ppb)	Ni (ppb)
10	341.8	13.66	0.0	6.96	138.4	99.39
40	1072	23.38	0.0	17.25	200.6	61.97
50	1404	67.85	0.0	34.63	204.6	72.62
60	1546	66.87	0.0	68.08	212.1	77.01
80	861.6	30.49	0.0	34.93	265.3	22.36
100	1264	31.28	0.0	32.38	290.0	29.68
120	1587	32.15	0.0	37.80	332.5	36.60
140	1668	31.37	0.0	29.23	367.6	21.05
170	2264	33.37	0.0	42.74	450.0	39.59
180	2193	30.84	0.0	42.93	406.7	36.47
210	2101	26.92	0.0	36.15	411.3	43.66
230	2677	33.47	0.0	39.36	482.2	56.45
260	3578	39.24	0.0	51.15	727.4	82.16
270	3657	37.79	0.0	45.44	692.8	88.08
290	4445	44.22	0.0	58.31	872.7	114.3
300	4695	45.36	0.0	64.42	998.0	121.1
320	4738	42.88	0.0	58.53	1064	127.1
340	5103	46.87	0.0	60.62	1196	135.9
360	5076	59.92	0.0	56.46	1213	131.6
380	5495	62.07	0.0	66.14	1389	145.5
390	5825	62.02	0.0	70.49	1488	150.9
400	6040	61.78	0.0	71.28	1651	161.4

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282 Conclusion

283 Five metals, selenium, arsenic, copper, iron, and nickel, which were constituents of the
 284 Pennsylvania coal combusted to generate the flue gas in the post-combustion CO₂ capture

process accumulated in the amine solvents used in the test. Generally, there was a gradual increase in the concentrations of most of these metals over the 200 – 400 hour test periods. Iron and nickel accumulation rates ranged from 8 – 25 ppb/hr for solvents A and B, but were lower for solvent C at 4 and 0.2 ppb/hr, respectively. For Solvent A, copper accumulated at a rate of 5 ppb/hr, and <0.5 ppb/hr for solvents B and C. Selenium accumulation rates were 5, 11, and 15 ppb/hr for Solvents A, B, and C, respectively. Arsenic was detected at very low concentrations and showed marginal build-up in all the three solvents tested, with accumulation rates of 0.1 - 0.2 ppb/ hr for all solvents. While mercury was detected in the uncombusted coal and in one of the solvents at a low levels, a trend of increasing solvent concentration could not be established in any of the solvents tested. The levels detected for iron and nickel could also result from corrosion of the stainless steel material from the process in addition to the coal. The trends for the accumulation of the metals were very similar for Solvents A and B, with some variation for Solvent C which also generally showed the lowest metals build-up. The levels detected were mostly in the parts per billion but over extended testing periods, further increase in the concentrations of these metals could require intermittent reclamation to reduce potential impacts on process.

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360 **Figure Captions**

361 Figure 1. Pilot unit for CO₂ capture.

362 Figure 2. Coal combustion unit for flue gas generation and SO₂ scrubbing unit.

363 Figure 3. Schematic of CO₂ capture process.

364 Figure 4. Selenium concentration accumulation in three amine solvents used for post-
365 combustion CO₂ capture.

366 Figure 5. Arsenic concentration accumulation in three amine solvents used for post-combustion
367 CO₂ capture.

368 Figure 6. Mercury concentration accumulation in three amine solvents used for post-combustion
369 CO₂ capture.

370 Figure 7. Copper concentration accumulation in three amine solvents used for post-combustion
371 CO₂ capture.

372 Figure 8. Iron concentration accumulation in three amine solvents used for post-combustion CO₂
373 capture.

374 Figure 9. Nickel concentration accumulation in three amine solvents used for post-combustion
375 CO₂ capture.