Toxic Substances from Coal Combustion - Forms of Occurrence Analyses

Technical Progress Report

Reporting Period Start Date: 4/30/96

Reporting Period End Date: 11/1/96 Semiannual Report

Sharon S. Crowley, Curtis A. Palmer, Allan Kolker, Robert B. Finkelman, Kathleen C. Kolb, and Harvey E. Belkin

December 6, 1996

DE-AI22-95PC95145

U.S. Geological Survey
National Center MS 956
Reston VA 20192

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Abstract

The overall objective of this project is to provide analytical support for the Physical Sciences, Inc. (PSI) effort being performed under DOE Contract No. DE-AC22-95101 and entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". The Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 program coals have been examined to determine the mode of occurrence of selected trace elements using scanning electron microscopy, microprobe analysis, and experimental leaching procedures. Preliminary microprobe data indicates that the arsenic content of pyrite grains in the Illinois No. 6 (0.0-0.027 ppm As) and Pittsburgh (0.0-0.080 ppm As) coals is similar. Pyrite grains observed in the Elkhorn/Hazard coal generally have arsenic concentrations (0.0-0.272 wt. % As) that are slightly higher than those of the Pittsburgh or Illinois No. 6 coals. One pyrite grain observed in the Elkhorn/Hazard coal contained much higher levels of arsenic (approximately 2 wt. % As). Preliminary microprobe analyses and data from leaching experiments indicate the association of arsenic with pyrite in the Pittsburgh and Illinois No. 6 coals. Leaching data for arsenic in the Elkhorn/Hazard coal, in contrast, is inconclusive and additional data are needed before a definite determination can be made.

Table of Contents

Introduction

The overall objective of the "Toxic Substances from Coal Combustion - Forms of Occurrence Analyses" project is to provide analytical support for the Physical Sciences, Inc. (PSI) effort being performed under DOE Contract No. DE-AC22-95101 and entitled "Toxic Substances From Coal Combustion - A Comprehensive Assessment". Project goals include (1) developing fundamental mechanistic data, and (2) determining models for the formation, partitioning, and emissions of toxic species from coal combustion. In support of this effort, the United States Geological Survey (USGS) will analyze a number of coal samples utilizing the techniques described below, to provide information necessary to achieve a better understanding of toxics behavior.

Phase I

As a complement to the analyses being performed by PSI under DOE Contract No. DE-AC22-95PC95101, data from a unique protocol developed by the USGS will be used to analyze selected coal size and density fractions for trace element forms of occurrence. In Phase I, the four Phase I coals will be analyzed. The protocol incorporates the elements described below.

All of the samples will be treated by a selective leaching procedure, a powerful technique for approximating modes of occurrence using differing combinations of solvents at various temperatures and concentrations. Splits of the coal will be leached with these solvents (ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid) according to the methods developed at the USGS. Results from these leaching tests will provide essential information on chemical bonding of the elements. Elements that are leached by hydrofluoric acid are generally associated with silicates, those that are leached by nitric acid are generally associated with sulfides, and those that are leached by hydrochloric acid are generally associated with carbonates.

Experiments also will be conducted to determine volatility of the elements by heating the coal samples to temperatures ranging from less than 200 ° C to more than 1,000 ° C. A split of each coal sample will be ashed using a low temperature ashing device. This procedure includes oxidation of the coal at temperatures of less than 200 ° C, resulting in a residue of unaltered minerals. This low temperature ash residue will then be chemically analyzed to determine the volatility of the elements at low temperatures. This information, in conjunction with other tests, will provide insight into chemical bonding of the elements present. The low temperature ash will then be used for semi-quantitative mineralogical determination by X-ray diffraction.

The above procedures provide indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. They will be complemented by direct procedures such as manual scanning electron microscopy (SEM) energy dispersive analysis (EDX) of polished pellets of coal. The advantage of the manual method over the automated, computer controlled SEM is that the operator can intelligently select the appropriate phases for analysis by EDX and the operator can apply instantaneous interpretation of the textural relations of the phases being analyzed. The mineralogical, geological, and geochemical expertise of the USGS personnel will provide unique and essential insights.

For a more sensitive and quantitative analysis, an electron microprobe analyzer will be used. Other, non-routine methods, such as analytical transmission electron microscopy and infrared spectroscopy, will be used as necessary.

The Agency shall not proceed with any of the work under the Phase II program until formal notification is provided.

Phase II

In Phase II, the Phase II coals will be analyzed. Detailed analysis of coal splits (size and density fractions) from both Phase I and Phase II coals will also be conducted, as required. The standard protocol to be used in Phase II is nearly identical to that used in Phase I; the only significant difference is in the samples to be analyzed. In Phase II, some samples may be subjected to separation procedures and subsequent analysis. For example, density or magnetic separations may be used, or handpicking of specific mineral grains. The protocol to be followed in Phase II incorporates the techniques described below.

Using a methodology similar to that of Phase I, all of the samples will be treated by a selective leaching procedure, using the solvents ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid. Results from these leaching tests will provide essential information on chemical bonding of the elements. Experiments to determine volatility of the elements will also be conducted by heating the coal samples to temperatures ranging from less than 200 ° C to more than 1,000° C, using the same procedures as described in Phase I.

These procedures provide indirect evidence, or approximations of the modes of occurrence of the trace elements in coal. As in Phase I, they will be complemented by direct determinations on polished pellets of coal using manual SEM analysis with the EDX analyzer . The mineralogical, geological, and geochemical expertise of the USGS personnel will provide unique and essential insights. For a more sensitive and quantitative analysis, an electron microprobe analyzer will be used. Other, non-routine methods, such as analytical transmission electron microscopy and infrared spectroscopy, will be used as necessary. Also in Phase II, some samples may be subjected to various separation procedures and subsequent analysis. For example, density or magnetic separations may be used or hand picking of specific mineral grains.

Methods

(1) Two of the program coals (the Pittsburgh and Elkhorn/Hazard coals) were received by the USGS and shipped to Geochemical Testing of Somerset, Pennsylvania in early May, 1996 for (1) grinding of samples to -20 mesh splits (samples later to be used in petrographic, SEM, and microprobe analysis), (2) grinding of samples to -60 mesh splits (samples to be analyzed by ICP-MS, ICP-AES, hydride generation, and cold vapor atomic absorption), and (3) analysis of sulfur forms. These splits

were returned by Geochemical Testing and shipped to the USGS, Denver, CO for chemical analysis. The Illinois No. 6 coal was received by the USGS and shipped to Geochemical Testing in early June, 1996, for grinding of samples (as described above) and for analysis of sulfur forms. This sample was returned by Geochemical Testing and shipped for chemical analysis to the USGS, Denver, CO on July 5, 1996. Sulfur form data for each of the three samples is in Appendix I.

(2) Chemical analyses (ICP-AES, ICP-MS) of the three raw coals have been completed.

(3) Representative splits of all program coal samples were ground and cast into pellets and polished for SEM and microprobe analysis according to the procedures outlined by ASTM, (1993) as modified by Pontolillo and Stanton (1994). The casting procedure impregnates, under pressure, approximately 7-8 grams of crushed sample with Armstrong C4 epoxy. The resultant mold is cured overnight at 60° C. A label is incorporated with the sample.

The pellet block is ground and polished using ASTM D2797-85 standards. The epoxy-coal pellet is ground with a 15 μm diamond platen and 600 SiC grit paper until flat and smooth. Rough polishing is done with 1 μm alumina and final polishing is completed with 0.06 μm colloidal silica. Ultrasonic cleaning between and after the various steps insures a final product relatively free of extraneous abrasive material.

Three pellets were prepared from each sample. Each pellet was sectioned with a thin, slow-speed diamond saw and carbon coated for SEM and microprobe analysis.

(4) Each of the three program coals was examined with the SEM with an attached energy dispersive X-ray analyzer (EDXA) to (1) determine major and minor mineralogy of the samples and (2) determine variations in morphology of pyrite grains. Mineral identifications using EDXA are tentative because of its semiquantitative capabilities; however, identification of minerals can be made based on morphology and cleavage characteristics of mineral grains. Because pyrite is known to be a primary source of arsenic in coal (Finkelman, 1994), differing pyrite morphologies were identified in the SEM analysis, for the selection of grains to be analyzed quantitatively with the microprobe. Two types of SEM's were used: an ETEC Autoscan and a JEOL 840[1]. Normal operating voltage was 20 KeV, both secondary electron and back-scattered modes were used.

(5) A fully-automated, 5 spectrometer instrument (JEOL JXA 8800L Superprobe[1]) was used to quantitatively determine element concentrations in sulfides by the wavelength-dispersive technique. In our preliminary microprobe work with the program coals, we measured the following elements: Fe, S, As, Ni, Cu, Zn, and Cd. Natural and synthetic standards were used. Beam current used was 2 x 10 -08 amps; voltage was 20 KeV. The probe diameter was set as a focused beam; the actual working diameter was about 3-5 micrometers. In this study, we considered the minimum detection limit for the microprobe to be at about 100 ppm for each of the elements analyzed, using counting times of 60 seconds for peak and 30 seconds for background for most of the elements. For arsenic, counting times of 90 seconds for peak and 45 seconds for background were used. Trace elements analyzed on the microprobe can be detected at this level; however, counting statistics have a large

uncertainty. In the probe analysis, we attempted to detect compositional differences among different pyrite morphologies. Microprobe data collected are shown in Appendix II.

(6) The sequential selective leaching procedure used in this study is similar to one described by Palmer et al. (1993) which was modified from Finkelman et al. (1990). Duplicate 5g samples were sequentially leached with 35 ml each of 1N ammonium acetate (CH_3COONH_3), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid (HNO_3) in 50 ml polypropylene tubes. Each tube was shaken for 18 hrs on a Burrell[b] wrist action shaker. Because of the formation of gas during some of the leaching procedures it was necessary to enclose each tube in two polyethylene bags, each closed with plastic coated wire straps that allow gas to escape but prevent the release of liquid. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis (INAA). The solutions were saved for inductively coupled argon plasma (ICP) analysis.

Results and Discussion

SEM and Microprobe Analysis

SEM analysis indicated the presence of the major minerals illite, kaolinite, quartz, and pyrite in each of the program coals (Appendix II). In addition to these four minerals, iron oxides were found in the Pittsburgh coal and calcite was found in the Illinois No. 6 coal. Minor and trace amounts of several other minerals were also observed. Differing morphologies for pyrite were observed in the program coals with the SEM; these morphologies included subhedral grains, euhedral grains, and framboids.

Microprobe analyses indicated that the arsenic content of pyrite grains in the Illinois No. 6 (0.0-0.027 ppm) and Pittsburgh (0.0-0.080 ppm) coals is similar, and that pyrites for these two coals are not distinguishable based on arsenic concentrations. The arsenic concentrations do not appear to vary according to morphology of pyrite grains; however, framboids were not well represented in the microprobe analysis due to their small size (15 micrometers in diameter or less) and difficulty in obtaining a good polish. In general, pyrite grains observed in the Elkhorn/Hazard coal have arsenic concentrations (0.0-0.272 wt. % As) that are slightly higher than those of the Pittsburgh or Illinois No. 6 coals. However, one grain of pyrite observed in the Elkhorn/Hazard coal (analyses 2.1, 2.2, and 2.3, 9/26/96; Appendix III) had a much higher level of arsenic (approximately 2 wt. % As). In future work, elemental mapping using the electron microprobe will be conducted to better characterize the distribution and mode of occurrence of the high arsenic pyrite grains in the Elkhorn/Hazard coal.

Nickel is generally low (0.0 to 0.067 wt. percent) in pyrite of all of the program coals. Two pyrite grains from the Elkhorn/Hazard coal contained higher levels of nickel (approximately 0.1 wt. percent).

---

[b]Use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U. S. Geological Survey.

Future microprobe work on the program coals will include broad beam microanalysis of organics to attempt to detect selenium, which is thought to be organically bound (Finkelman, 1994). Other work will involve using SEM image analysis to help determine the distribution of As, Se, or Cr. All data will be used in mass balance calculations of trace element residence.

Leaching Experiments

Leaching experiments were completed for the three program coals and the resulting samples (leachate solutions and solid residues) were submitted for chemical analysis. ICP-AES and ICP-MS data (for leachate solutions) and INAA data (for solid residues) have been obtained. The chemical data for leachates have been processed to derive the mean percentages of each element leached by the four leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of each element in the raw coal (Table 1). The calculated percentages were then used as an indirect method for determining the mode of occurrence of specific trace elements in the coals. We estimate an error of ±25 percent for these data. The calculated percentages in Table 1 are preliminary and subject to revision as new data become available.

Aluminum and potassium are strongly leached by hydrofluoric acid in each of the three program coals; these data suggest an association of aluminum and potassium with silicates (probably kaolinite and illite). Iron is almost entirely leached by nitric acid in the Pittsburgh and Illinois No. 6 coals, indicating the association of iron with pyrite in these samples. Sulfur form analyses corroborate the presence of pyritic sulfur (0.91-1.57 percent; Appendix I) in these coals. In contrast, iron is leached primarily by hydrochloric acid in the Elkhorn/Hazard coal. The data perhaps indicate that oxidation of pyrite occurred with the formation of leachable iron oxides or sulfates. Additional data are necessary before an evalution can be made. Although the leaching percentages indicate that a very small amount of silicon was leached in each of the three program coals, these calculations are misleading because silicon is lost during the drying process used to prepare the leachate samples for ICP-MS and ICP-AES analysis.

Because arsenic in the Pittsburgh and Illinois No. 6 coals was leached primarily by nitric acid, we infer the association of arsenic with pyrite. The association of arsenic with pyrite in these coals is confirmed by microprobe analyses. In the Elkhorn/Hazard coal, arsenic behaves in a manner similar to that of iron; arsenic is leached primarily by hydrochloric acid. It is possible that pyrite grains with high concentrations of arsenic (approximately 2 wt. percent) in the Elkhorn/Hazard were more readily oxidized than grains with low concentrations of arsenic (100 ppm arsenic). However, the arsenic data are incomplete, as indicated by low total percentages for arsenic in the four leachates (about 40 percent) and additional data are needed before a definite determination can be made. Future work may involve the examination of solid residue from the nitric acid leach to determine if some of the arsenic was not leached.

Conclusion

Phase I of the project is progressing satisfactorily. The USGS has analyzed the three program coals (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6) by using (1) trace element analysis (ICP-AES, ICP-MS, Cold Vapor Atomic Absorption, Hydride Generation), (2) leaching experiments, (3) preliminary SEM analysis, and (4) preliminary microprobe analysis.

References

ASTM (American Society for Testing and Minerals), 1993, Annual Book of ASTM Standards. Vol. 5.05 Gaseous Fuels, Coal and Coke. Philadelphia, PA, 526 pp.

Finkelman, R.B. Palmer, C.A., Krasnow, M.R., Aruscavage, P.J. Sellers, G.A., and Dulong, F.T., 1990, Combustion and leaching behavior of elements in Argonne Premium Coal Samples: *Energy and Fuels* 4(5) 755-766.

Finkelman, R.B., 1994, Modes of occurrence of potentially hazardous elements in coal: Levels of confidence: *Fuel Processing Technology* (39) 21-34.

Palmer, C.A., Krasnow, M.R., Finkelman, R.B., and D'Angelo, W.M., 1993, An evaluation of leaching to determine modes of occurrence of selected toxic elements in coal: *Journal of Coal Quality* 12 (4) 135-141.

Pontolillo, J. and Stanton, R.W., 1994, Coal petrographic laboratory procedures and safety manual II. *U. S. Geological Survey Open-File Report 94-631*, 69 p.

Table 1. Mean percentages of each element leached by various leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of the element in the raw coal (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6). We estimate an error of ±25 percent for these data. All data are preliminary and subject to revision as new data become available. Am. Ac.=ammonium acetate. Raw coal analyses are in ppm (whole coal basis).

	Al	Ca	Fe	K	Mg	Mn	Na	Si	Ti
Pittsburgh									
Raw Coal (ppm)	8113	2347	9190	787	382	13	542	14332	407
Am. Ac.	0	75	0	1	40	40	54	0.7	0
HCl	2	18	4	2	7	1[illegible]	18	0.4	0
HF	92	4	6	131	41	12	47	0	36
HNO_3	1	3	106	0	0	42	8	0.1	0
Elkhorn/Hazard									
Raw Coal (ppm)	12702	1257	3245	929	323	14	320	18323	719
Am. Ac.	0	49	1	3	21	31	54	1	0
HCl	2	19	44	6	16	62	14	0	0
HF	54	6	15	101	45	11	71	0	18
HNO_3	0	1	3	0	0	0	25	2	0
Illinois No. 6									
Raw Coal (ppm)	9812	2797	12967	1539	540	37	436	22629	562
Am. Ac.	0	84	0	3	13	41	42	0	0
HCl	1	5	7	3	6	10	13	0	0
HF	58	2	4	74	20	4	37	0	31
HNO_3	1	3	98	1	8	19	17	0	0

Table 1. (Continued) Mean percentages of each element leached by various leaching agents (ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid) compared to the original concentration of the element in the raw coal (Pittsburgh, Elkhorn/Hazard, and Illinois No. 6). We estimate an error of ±25 percent for these data. All data are preliminary and subject to revision as new data become available. Am. Ac.=ammonium acetate. Raw coal analyses are in ppm (whole coal basis).

	As	Cd	Co	Cr	Cu	Ni	Pb	Sb
Pittsburgh								
Raw Coal (ppm)	4.7	0.06	2.4	8.8	5.3	6.6	3.1	0.29
Am. Ac.	1	11	0	0	9	10	23	5
HCl	11	29	15	35	27	200	39	11
HF	5	20	0	43	7	25	12	19
HNO_3	57	44	35	55	75	165	60	28
Elkhorn/Hazard								
Raw Coal (ppm)	5.1	0.06	7.0	14.4	19.2	12	8.8	1.2
Am. Ac.	1	25	0	0	3	10	10	1
HCl	29	56	9	15	25	25	41	3
HF	6	36	0	24	0	12	6	15
HNO_3	4	8	0	5	4	16	11	6
Illinois No. 6								
Raw Coal (ppm)	3.1	0.41	3.6	18.5	8.2	12.4	13.4	0.4
Am. Ac.	1	1	7	0	3	9	15	2
HCl	19	25	37	9	11	26	32	5
HF	5	4	0	20	8	12	7	9
HNO_3	40	39	29	16	77	104	30	27

Appendix I. Sulfur Form Data (all data in percent on a dry basis).

	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur	Total S
Pittsburgh	0.01	0.91	1.20	2.12
Elkhorn/Hazard	0.03	0.12	0.72	0.87
Illinois No. 6	0.04	1.57	2.21	3.82

Appendix II. Mineralogy of the three program coals based on SEM analysis.

Pittsburgh

Major:	Illite, kaolinite, quartz, pyrite, iron oxide
Minor/trace:	Barite, TiO_2, calcium sulfate (probably gypsum)

Elkhorn/Hazard

Major:	Illite, kaolinite, quartz, pyrite
Minor/trace:	Iron oxide, chalcopyrite, TiO_2, barite, apatite, monazite (REE phosphate), zircon.

Illinois No. 6

Major:	Illite, kaolinite, quartz, pyrite, calcite
Minor/trace:	none observed

Appendix III. Quantitative microprobe analyses of pyrite grains in the Pittsburgh, Elkhorn/Hazard, and Illinois No. 6 coals. Subh.=subhedral, euh.=euhedral, irr.= irregular, fram.=framboid, n.d.=no data, no.=analysis number.

Pittsburgh Coal

No.	Date (1996)	Pellet	Morph. of pyrite	Size (μm)	Total (wt.%)	As (wt.%)	Cu (wt.%)	Ni (wt.%)	Zn (wt.%)
2.3	11-26	altB	subh.	60x80	96.056	0.08	0	0	0.012
3.1	11-26	altB	euh.	60x60	98.11	0.005	0	0	0.004
3.2	11-26	altB	euh.	60x60	98.6	0.002	0	0.003	0.013
3.3	11-26	altB	euh.	60x60	98.36	0.0	0.01	0.016	0
4.1	11-26	altB	subh.	40x60	96.85	0.0	0	0	0
4.2	11-26	altB	subh.	40x60	97.84	0.004	0	0	0
5.1	11-26	altB	subh/irr.	25x60	97.24	0.011	0.013	0	0
5.2	11-26	altB	subh/irr.	25x60	97.69	0	0	0	0
6.1	11-26	altB	subh/irr.	60x100	99.37	0	0	0.009	0
6.2	11-26	altB	subh/irr.	60x100	97.37	0.004	0	0	0
6.3	11-26	altB	subh/irr.	60x100	98.97	0.009	0	0	0
7.1	11-26	altB	euh.	120	98.46	0.003	0.028	0.001	0
7.2	11-26	altB	euh.	120	100.43	0.012	0.001	0.055	0
8.1	11-26	altB	cleat?	20x60	96.75	0.0	0	0.016	0
8.2	11-26	altB	cleat?	20x60	97.86	0.0	0	0.002	0
9.1	11-26	altB	cleat?	15x70	98.17	0.016	0.016	0.013	0.003
9.2	11-26	altB	cleat?	15x70	99.55	0.023	0	0	0.011
10.1	11-26	altB	cleat?	100	99.28	0.005	0.003	0	0
10.2	11-26	altB	euh.	100	98.7	0.0	0.023	0.016	0
10.3	11-26	altB	euh.	100	97.82	0.001	0.032	0.006	0.014
13.1	11-26	altB	euh.	20	98.39	0.026	0.189	0.001	0.017

Elkhorn/Hazard

No.	Date (1996)	Pellet	Morph. of pyrite	Size (μm)	Total (wt.%)	As (wt.%)	Cu (wt.%)	Ni (wt.%)	Zn (wt.%)
1.1	11-26	altB	irr.	40x60	95.41	0.128	0.013	0	0
2.1	11-26	altB	irr.	10x20	95.84	0.019	0.017	0.007	0
3.1	11-26	altB	framb.	10	95.92	0.124	0.024	0.038	0.002
4.1	11-26	altB	irr.	30	97.4	0.017	0.034	0.041	0
4.2	11-26	altB	irr.	30	98.33	0.021	0.038	0.15	0
5.1	11-26	altB	framb.	20	97.03	0.013	0.012	0.021	0
5.2	11-26	altB	framb.	20	95.72	0.04	0.013	0.025	0
6.2	11-26	altB	framb.	30	96.03	0.053	0.006	0.102	0
7.1	11-26	altB	subh.	15	96.06	0.011	0.063	0	0
8.1	11-26	altB	cleat?	5x30	98.13	0.272	0	0	0
9.1	11-26	altB	subh.	70x80	98.06	0.009	0.028	0	0
9.2	11-26	altB	subh.	70x80	96.75	0.00	0	0	0
10.1	11-26	altB	subh.	80x100	98.88	0.013	0.011	0	0
10.2	11-26	altB	subh.	80x100	100.2	0.0	0.001	0	0
10.3	11-26	altB	subh.	80x100	99.12	0.011	0	0	0
11.1	11-26	altB	subh.	30x40	96.52	0.0	0	0.016	0
12.1	11-26	altB	sub/euh.	20x35	96.79	0.024	0.022	0.003	0.011
12.2	11-26	altB	sub/euh.	20x35	96.57	0.012	0	0.001	0
2.1	9-26	B	sub/euh.	30x50	98.85	1.799	0.002	0.002	n.d.
2.2	9-26	B	sub/euh.	30x50	98.71	1.971	0.006	0	n.d.
2.3	9-26	B	sub/euh.	30x50	98.66	2.1	0	0	n.d.

Illinois No. 6

No.	Date (1996)	Pellet	Morph. of pyrite	Size (μm)	Total (wt.%)	As (wt.%)	Cu (wt.%)	Ni (wt.%)	Zn (wt.%)
1.1	11-26	altB	subh.	50x60	97.48	0.002	0.026	0.048	0
1.2	11-26	altB	subh.	50x60	98.03	0.027	0.002	0.042	0.022
1.3	11-26	altB	subh.	50x60	98.24	0.012	0.016	0.04	0
2.1	11-26	altB	framb.	25	98.01	0.008	0.008	0	0
3.1	11-26	altB	framb.	20	96.11	0	0.028	0.013	0
4.1	11-26	altB	cleat?	20x70	100.13	0	0	0	0
4.2	11-26	altB	cleat?	20x70	100.31	0	0	0	0
7.1	11-26	altB	framb.	20	99.59	0.011	0.002	0	0
11.1	11-26	altB	subh.	20	100.34	0	0	0.008	0
12.1	11-26	altB	framb.	30	98.23	0.014	0.011	0.003	0
12.2	11-26	altB	framb.	30	98.59	0	0	0.012	0
13.1	11-26	altB	euh.	10	95.7	0	0.077	0.067	0.003
14.1	11-26	altB	framb.	20	97.22	0.002	0.012	0.063	0