American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

Chemical composition of coal and other mineral slags

LLOYD E. STETTLER , HARRY M. DONALDSON & GEORGE C. GRANT

To cite this article: LLOYD E. STETTLER , HARRY M. DONALDSON & GEORGE C. GRANT (1982) Chemical composition of coal and other mineral slags, American Industrial Hygiene Association Journal, 43:4, 235-238, DOI: 10.1080/15298668291409668

To link to this article: https://doi.org/10.1080/15298668291409668

The trace element contents of eighteen coal, copper, and nickel slags were determined by proton induced x-ray emission (PIXE) and atomic absorption spectrophotometry. Varying amounts of the suspect carcinogens, beryllium, chromium, nickel, and arsenic were found in the slags. As a class, the coal slags contain the lowest quantities of these elements while the slags from secondary copper smelters contain the greatest quantities.

Chemical composition of coal and other mineral slags

LLOYD E. STETTLER[A], HARRY M. DONALDSON[B] and GEORGE C. GRANT[C]
[A]Division of Biomedical and Behavioral Science, National Institute for Occupational Safety and Health,
4676 Columbia Parkway, Cincinnati, Ohio 45226; [B]Division of Surveillance, Hazard Evaluations and Field
Studies, National Institute for Occupational Safety and Health, [C]College of William and Mary, Virginia
Associated Research Center, Newport News, Virginia 23606

introduction

In the later part of the 19th century, steel came into general use as a material for the fabrication of large structural items such as ships, bridges, railroad cars, etc. These steel structures when exposed to the weather would corrode and required a protective coating of paint to prevent rusting. The periodic maintenance of these structures required that the surfaces be cleaned of rust and loose paint in order to obtain a surface that would accept a new protective coating. The usual method of preparing these surfaces has been by abrasive blasting with sand.

In studying the incidence of silicosis in Great Britain in the 1930's it was found that most workers in the dusty trades were prone to silicosis. The average employee worked in these industries for 40.1 years, and the average age at death was 54.1 years. A sand blaster, however, was found on the average to work for only 10.3 years and the average age at death was 40.7 years.(1) With the recognition of this hazard, Great Britain in 1950 banned the use of silica sand as an abrasive blasting material.(2) This was followed by efforts to restrict the use of sand for abrasive blasting purposes in Germany and the Netherlands, which led to research in Germany to find less toxic substitute abrasive blasting materials.(3) In considering candidate materials as substitutes for sand three properties were sought: (1) the material should be below 1% in free silica, (2) the material should possess good abrasive properties, and (3) the materials should be competitive economically with sand. Mineral slags such as copper slag and chromium slag were found to have these desired properties.(3) However, potential health problems other than silicosis which may be associated with these materials were not considered.

The mineral slags are metallurgical waste products resulting from smelting operations in which metals such as copper, nickel, chromium, etc. are recovered. In the smelting process, a two phase liquid system exists with a molten slag phase floating on top of molten metal. The molten slag is drawn off and run into water to convert it to a frit which can be conveniently handed for disposal purposes. Since the fritting process usually produces a hard, small, sharp particle, many of the frits were found to have abrasive properties.

In addition to mineral slags, large quantities of a wet bottom boiler slag produced in certain types of coal fired electric utility boilers in the United States has found use as an abrasive blasting material. This slag is formed during the burning of a powdered coal which produces an ash with a relatively low melting point. During the burning process, this molten ash falls to the bottom of the furnace as a viscous liquid which is then allowed to drop into water where it frits. The resulting product is a hard black solid with less than 1% free silica and is an excellent abrasive blasting material.

A recent study in this laboratory investigated the fibrogenic potentials of two of these slag materials, one copper and one coal slag.(4) The coal slag was found to induce fibrosis while the copper slag did not. Chemical analyses of these two slags determined the presence of varying amounts of trace metals such as beryllium, chromium, nickel, and arsenic that are considered suspect carcinogens.(5) In this report, the trace element concentrations of eighteen slag materials are presented.

materials and methods

Of eighteen slags used in this study, twelve were derived from coal. Four of these coal slags are used in abrasive blasting and were obtained from commercial suppliers. The remaining eight coal slag samples were obtained directly from coal fired power plants. The commercial availability of these eight samples is unknown.

Five of the six remaining samples were copper slags. Three of the copper slags were from primary smelters, two of which were from the same smelting operation and ore source but processed at different times (1976 and 1977). These two slags have been used commercially whereas utilization of the third is unknown. The two remaining copper slags were from a secondary smelting operation and were obtained from a commercial supplier, one sample in 1974, the other in 1978. The other sample analyzed was a nickel slag. The utilization of this sample in commerce is unknown.

The slag samples were analyzed by atomic absorption spectrophotometry and proton induced x-ray fluorescence

TABLE I
Coal Slag Trace Analyses ($\mu g/g$)

Element	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11	No. 12
Be	29±3	7±3	48±3	24±3	30±2	29±3	<8	<6	27±4	<4	40±3	33±4
Ti	10 000±2000	5300±200	5300±300	4900±600	3400±600	3400±400	7100±700	2300±300	3100±400	3600±700	4300±300	3300±400
V	400±100	270±80	320±80	330±70	180±50	190±50	<400	<200	<200	<200	<180	<180
Cr	200±40	<100	<120	<120	<150	<150	<100	110±30	130±40	180±40	<210	<180
Mn	600±100	<200	<200	<200	390±80	360±90	290±80	170±30	<140	240±60	<180	<200
Ni	70±10	<40	70±20	70±10	40±10	51±8	26±7	18±5	45±8	20±5	<60	33±9
Cu	49±8	21±4	50±10	22±5	8±2	<6	70±4	27±6	13±3	28±5	52±4	12±4
Zn	140±30	36±4	190±6	86±8	87±3	67±3	35±3	13±4	105±7	30±3	51±6	100±9
Ga	9±2	9±3	9±3	10±2	<6	<8	8±3	6±2	<4	<4	27±5	13±3
As	10±2	<8	18±2	7±2	<4	5±2	4±1	<10	<4	<4	<10	<6
Se	<2	<6	<4	<4	<4	<2	<2	<2	<4	5±1	<4	<6
Rb	85±3	61±5	108±4	87±6	65±3	64±3	31±8	80±3	75±3	34±5	54±4	68±30
Sr	780±10	540±10	295±8	223±5	218±4	210±10	4600±200	1710±20	433±9	3600±200	1460±20	530±10
Sc	1700±500	500±100	600±200	800±200	600±200	600±200	<1800	<800	<400	<1600	<600	400±100
Y	36±5	45±4	52±6	43±6	40±9	35±3	37±5	40±10	34±3	41±4	65±6	45±2
Zr	178±10	189±8	186±8	150±5	145±4	147±4	270±3	170±10	146±6	240±10	184±9	146±5
Nb	13±2	24±3	21±5	14±4	12±2	12±2	12±2	14±3	14±4	10±3	14±3	11±3
Mo	<8	<8	<18	<6	<12	<4	<6	<6	<8	<4	<6	11±4
Ba	1840±100	400±100	900±200	510±100	400±150	400±100	4700±300	4200±200	1200±100	9900±800	1900±100	710±100
Pb	<12	<15	20±4	<10	<10	<6	<8	<6	<8	<10	<10	<12

(PIXE). Beryllium, sodium, magnesium, and aluminum were analyzed by atomic absorption spectrophotometry using a Perkin-Elmer Model 360 atomic absorption spectrophotometer. Conventional flame atomization with air-acetylene was used for the sodium, magnesium, and aluminum analyses. Electrothermal atomization using a Perkin-Elmer Model HGA 2100 graphite furnace and AS-1 autosampler was used for the beryllium analyses. Atomization was performed without chemical separation using pyrolytically coated graphite tubes treated with lanthanum to prevent carbide formation in a procedure similar to that described by Runnels.(6) All elements with atomic numbers greater than 13 (silicon through uranium) were determined simultaneously for each sample by PIXE analysis.

The following procedures were used to prepare the slag samples for analysis. Approximately one gram of each sample was ground into a fine powder using an agate mortar and pestle. A 50 mg sub-sample of each slag was added a to Teflon beaker. Ten mL of double distilled HNO_3 was then added (cold) to each sample with subsequent heating for several hours at 120 °C. Five mL of HF was then added and the samples were simmered at 95 °C for 24 hours. After cooling, 30% H_2O_2 was added as necessary to any samples containing undigested material. The samples were then taken twice to *near* dryness followed by warming with 5 mLs of concentrated HCl. This step minimizes excess fluoride which would otherwise degrade detection limits due to interaction of high energy photons with detector circuits. After complete digestion, the samples were taken to final volume by removing the watch glasses, warming the solutions, and doping with a known concentration of indium which served as an internal standard for the PIXE analysis. A portion of each final volume was then used for the atomic absorption analysis after dilution 11X with deionized water. Procedure blanks and NBS Fly Ash (SRM 1633) were prepared along with samples. All reagents are purified and monitored in-house.

PIXE targets were prepared by micropipetting droplets of the final solutions onto polycarbonate films in a clean room. Targets were dried in an infrared oven. At least two targets were prepared for each analyte. In addition, as a check on digestion losses, PIXE powder targets were prepared by spreading a few mg of each sample over a known surface area and analyzed by comparison to a powdered external standard (USGS AGV-1 and GSP-1). Although this method is not as precise as the internal standard method it serves as a useful check and also determines the presence of indium which would necessitate use of a different internal standard. Additional details for sample preparation, target analysis, and extensive PIXE calibration with a variety of standards and standard reference materials are given elsewhere.(7)

TABLE II
Summary of the Analyses for the Twelve Coal Slag Samples

Element	Number of Coal Slags Containing the Element	Range of Values in $\mu g/g$
Be	9	7 - 48
Ti	12	2300 - 10 000
V	6	180 - 400
Cr	4	110 - 200
Mn	6	170 - 600
Ni	10	18 - 70
Cu	11	8 - 70
Zn	12	13 - 190
Ga	8	6 - 27
As	5	4 - 18
Se	1	5
Rb	12	31 - 108
Sr	12	210 - 4600
Sc	7	400 - 1700
Y	12	34 - 65
Zr	12	145 - 270
Nb	12	10 - 24
Mo	1	11
Ba	12	400 - 9900
Pb	1	20

results

All of the slag materials analyzed are silicates whose principal metallic components are sodium (0.2% to 3.2%), and magnesium (0.5% to 2.2%), aluminum (0.9% to 7.1%), potassium (0.1% to 3.4%), calcium (0.2% to 13.6%), and iron (3.3% to 23.0%). The trace element concentrations for the slags are given in Tables I through III. The values presented represent the average of two analyses with the standard deviation. All other elements were present below PIXE detection limits. Comparison of PIXE powder targets (results not shown) with the digested samples showed no significant losses for any element detected.

Contamination in procedural blanks was negligible with respect to all elements except zinc where a *slight* elevation (less than 25%) in the determined values may have occurred in two samples with low zinc. Analysis of NBS Fly Ash for beryllium resulted in a value of 14 ± 3 ppm Be compared with an estimated value (NBS) of 12.

discussion

The analytical results indicate that the slags contain varying quantities of potentially hazardous elements. These elements include beryllium, chromium, nickel, and arsenic, all of which are considered by NIOSH as carcinogens or suspect carcinogens.

In general, the coal slags contain the lowest concentrations of the suspect carcinogens (Table I). However, nine of the twelve coal slags analyzed do contain beryllium, ranging from 7 to 48 μg/g. Most coal found in the United States contains traces of beryllium.(8) Therefore, the presence of beryllium in these coal slags is not surprising. Chromium was found in only four coal slags ranging from 110 to 200 μg/g while ten coal slags contained nickel in concentrations 18 to 70 μg/g. Arsenic in 4 to 18 μg/g quantities was found in five coal slags. The coal slag with the highest arsenic content (18 μg/g) was the only coal slag that also contained lead, 20 μg/g.

The trace element concentrations of the primary copper slags (Table III) are very dependent upon the ore being smelted. Primary copper slags Nos. 1 and 2 were from the same ore sources but were processed at different times. The trace element concentrations of these two slags are nearly identical with no beryllium, chromium, or nickel being detected in either sample and nearly equal amounts of arsenic (32 and 34 μg/g) present in both samples. However, primary copper slag No. 3, which was from a different ore source and smelter, contained large amounts of chromium (340 μg/g) and arsenic (1450 μg/g). No beryllium or nickel was detected in this sample, but a large amount of lead (1220 μg/g) was found.

The secondary copper slags contained the largest quantities of beryllium (125-180 μg/g), chromium (2100-2400 μg/g), nickel (2200-2440 μg/g), and lead (6600-8900 μg/g). While little variation in trace element concentrations was seen in the two analyzed samples, it would normally be expected that such slags would vary considerably in composition since various scrap metal sources would be used in the smelting operations which generate these slags.

The one nickel slag examined was found to contain significant amounts of chromium (3700 μg/g) and nickel (1400 μg/g).

The analytical results presented in the report have identified the presence of carcinogens or suspect carcinogens, as well as other toxic elements in the coal and mineral slags

TABLE III
Mineral Slag Trace Analyses (μg/g)

Element	Copper Primary Smelter No. 1	Copper Primary Smelter No. 2	Copper Primary Smelter No. 3	Copper Secondary Smelter No. 1	Copper Secondary Smelter No. 2	Nickel Primary Smelter
Be	<40	<6	<6	125±10	180±10	<6
Ti	1200±100	1200±100	1800±300	1500±400	1500±100	250±70
V	<80	<80	<180	160±50	<80	<60
Cr	<60	<40	340±90	2100±300	2400±100	3700±200
Mn	1700±100	2000±100	<400	2400±400	1400±200	1100±100
Ni	<18	<18	<20	2200±300	2240±70	1400±100
Cu	1340±20	1460±40	4200±400	6400±700	5000±200	17±2
Zn	141±4	133±4	26 000±2000	52 000±6000	18 900±500	75±2
As	32±10	34±2	1450±60	<40	<40	<2
Se	<6	<4	<8	32±7	18±5	<2
Br	10±2	9±1	<10	<14	<12	5±1
Rb	10±2	9±1	<12	<8	<6	<2
Sr	208±4	188±8	151±10	120±10	77±5	5±1
Sc	<800	<1000	500±100	500±200	<400	<200
Y	20±2	18±1	<8	27±9	<20	<2
Zr	300±20	50±4	69±6	850±50	264±8	15±2
Nb	<4	<6	<6	24±7	19±5	<2
Mo	<4	<6	480±10	240±10	160±20	<2
Sn	<18	<20	60±10	1000±60	1260±30	15±5
Sb	40±10	<18	500±40	<40	<20	<12
Ba	550±90	470±80	<80	500±100	700±200	<60
Pb	9±3	<6	1220±70	6600±500	8900±100	<4

tested. These analyses show only the presence of these materials and not their chemical combination states which may alter their toxicity. Further work is needed to evaluate the health and safety aspects of these slags. This work should include the collection of exposure data during actual use of the slags, experiments such as solubility studies to determine the biological availability of hazardous elements present in the slags, and long term inhalation studies using appropriate animal models. However, given the large variations in trace element content of the various slags, testing of one slag of a particular type may not be sufficient to assess the safety of all slags of that type. Quality control to minimize and/or standardize the acceptable amounts of trace elements in the slags may be necessary.

references

1. **Merewether, E.R.A.**: The Risk of Silicosis in Sand Blasters. *Tubercle 17*:345-391 (1936).
2. Factory Act 1937 and 1948 — Blasting (Casting and Other Articles) Special Regulations, 1949 (SI 1949, No. 2225) London, Ministry of Labor and National Service, Factory Dept. 1951, pp. 4331-4335.
3. **Gesell, W.**: Replacement of Quartz Sand in Pneumatic Blasting Operations by Mineral Blasting Media That Do Not Cause Silicosis. *Stahl U. Eisen 86 No. 14*:906-912 (1966).
4. **Mackay, G.R., L.E. Stettler, C. Kommineni and H.M. Donaldson**: Fibrogenic Potential of Slags Used as Substitutes for Sand in Abrasive Blasting Operations. *Am. Ind. Hyg. Assoc. J. 41*:836-842 (1980).
5. **Christensen, H.E., E.J. Fairchild and R.J. Lewis**: *Suspect Carcinogens*, 2nd Ed. DHEW(NIOSH) Publication No. 77-149. 251 pp. (1977).
6. **Runnels, J.H., R. Merryfield and H.B. Fisher**: Analysis of Petroleum for Trace Metals — A Method for Improving Detection Limits for Some Elements with the Furnace Atomizer. *Anal. Chem. 47*:1258-1263 (1975).
7. **Jolly, R.K., G.C. Grant, *et al.***: Simultaneous Analysis of 48 Elements in Biological Samples by Proton Induced X-ray Emission (PIXE). Manuscript in preparation.
8. **Stadnichenko, T., P. Zubovic and N.B. Sheffey**: *Beryllium Content of American Coals*, Geological Survey Bulletin, 1954-7. Govt. Printing Office, Washington, D.C. (1961).

Call for professional development course monitors

Approximately 200 monitors are needed for the Professional Development Courses at the 1982 AIH Conference in Cincinnati. In addition to the satisfaction of serving fellow members, monitors receive complimentary admission to the course(s) being monitored.

Courses are offered at various times from 1-5 p.m. on Sunday and Monday afternoon, June 6 and 7, 1982.

Interested individuals should contact John Conti, AIHA, 475 Wolf Ledges Pkwy., Akron, OH 44311-1087 (216) 762-7294.