



Project Summary

Trace Element Characterization of Coal Wastes—Fifth Annual Progress Report

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During the past year we continued our research on environmental control technologies as they relate to coal preparation wastes and extended our assessments to include studies of high-sulfur Appalachian coal cleaning wastes.

The most promising control technology for dealing with high-sulfur coal wastes consists of sequential slurry coating of the waste with lime and limestone. In the configuration tested (0.35% lime and 1.1% limestone), this technique controlled the waste effluent quality for 4 months; the effluent pH remained between 7.3 and 7.6, and the trace element concentrations (Al, Ca, Mn, Fe, Co, Ni, Cu) were reduced by 40 to 99-plus %. Codisposal of coal wastes and alkaline soils or mine overburdens is partly effective in controlling the leachate quality under steady-state conditions. However, none of the materials tested could control the highly acidic effluents obtained under intermittent leaching conditions.

Comparisons between trace element concentrations predicted by chemical equilibrium models and those obtained in experiments with coal waste leachates yielded good agreements for the major cations (Al, Ca, Fe) but, except for fluoride, the major

anions were not well accounted for. The observed trace element concentrations were all significantly lower than predicted.

Calcination experiments have shown that high-sulfur coal waste from Appalachia (Plant K) behaves differently than other wastes we have studied. The high cost of this technology (\$1.39 to \$9.84/ton product) places it outside the realm of economic feasibility at this time.

We have also completed an assessment of the Plant K coal wastes. These materials are similar to those from the Illinois Basin and their leachates are often very acidic, with pH values sometimes less than 2. Several trace elements have shown discharge severities greater than unity (Fe, As, Ni, Mn, Al), but iron is by far the worst offender, with values sometimes greater than 100.

Results of the EPA extraction procedure, used to classify solid wastes under the Resource Conservation and Recovery Act, compare favorably with those of our own leaching experiments for those elements analyzed (Ag, As, Ba, Cd, Cr, Hg, Pb, Se). However, coal wastes release substantial quantities of other trace elements not included in the protocols at present (Fe, Al, Ni, Mn, Zn, Cu).

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

In the past, our research on coal and coal wastes focused on identifying trace elements released in hazardous amounts during weathering and leaching of high-sulfur coal refuse from the Illinois Basin, and on evaluating control technologies for this problem. Present efforts are directed toward further development of these control technologies and extension of trace element assessments to the drainages from high-sulfur coals and coal wastes from Appalachia.

The drainages from many coal waste dumps are often highly contaminated with trace or inorganic elements. However, until recently there has been little concrete information on the quantities released, the controlling chemistry involved, or the ways to control these releases. Accordingly, the principal objectives of our program are to:

- (1) Assess the nature and magnitude of trace element releases of environmental concern.
- (2) Reveal experimentally the chemistry controlling trace element releases.
- (3) Evaluate and recommend appropriate pollution control technologies or necessary research and development programs.

The studies under way are a continuation of experimental efforts begun in 1976, which were directed toward identifying and quantifying the trace element releases from high-sulfur coal wastes from the Illinois Basin. We now have a good quantitative understanding of the environmental concerns associated with these wastes and their drainages. In FY 1979 we began in-depth experimental evaluations of various technologies for controlling them. Among the methods considered were codisposal of the coal waste with neutralizing or attenuating agents, containment of waste leachates coupled with water treatment techniques, and alteration of the waste to yield an environmentally inert material. Cost analysis showed the last of these technologies to be too costly, while the first two were

only partially effective, at least in the configuration studied. In FY 1980 we have continued to evaluate and improve these technologies, emphasizing those we consider to be the most promising; namely, sequential slurry treatment of the coal waste with lime and limestone and certain codisposal techniques. We also extended our trace element assessments to include coals and coal wastes from Appalachia.

Technical accomplishments of FY 1980 fall into three general areas: (1) studies of control technologies for high-sulfur coal wastes from the Illinois Basin, (2) evaluation and assessment of coal wastes from Appalachia, and (3) continuing development of procedures and techniques.

Environmental Control Technologies

Studies performed over the past several years show that the drainages from uncontrolled piles of high-sulfur coal wastes typically are very acidic (pH values less than 2 have been observed) and contain environmentally significant concentrations of several trace elements. This contamination is caused by sulfuric acid generated within the waste to oxidation of pyrite. To eliminate the contamination one must prevent the formation of the acid within the waste, neutralize the acid *in situ* after it is formed, or allow the leaching to take place and treat the effluents to remove the acid and trace element contaminants. Each of these approaches has advantages and disadvantages.

Acid formed in a waste pile can be neutralized *in situ* by mixing the coal refuse with alkaline materials either before or during disposal. We have demonstrated that if the pH of the waste effluents is maintained in the proper range, the trace element concentrations also stay within acceptable limits. The initial pH of the waste effluent can be easily controlled by adding hydrated lime to the waste, but this treatment is only temporary because any excess lime is quickly washed out of the solid refuse. Ground limestone is more durable, since it is not soluble in neutral solutions, but it cannot control the high initial acidities of high-sulfur coal waste. Although neither the lime treatment nor the limestone treatment alone is an adequate control technology, a combination of the two, using a small amount of lime to control the initial acidity and a larger

amount of limestone to control the slowly generated acid within the pile, promises the advantages of both without the limitations of either. Experiments completed during FY 1980 show that this approach is very effective in controlling coal waste effluents for up to 4 months.

Leachates from high-sulfur coal wastes obtained from the Illinois Basin (Plant B) typically have pH values of approximately 2.0 or less when subjected to long-term laboratory weathering experiments. However, when the same wastes were sequentially treated with 0.35% lime and 1.0% limestone and subjected to artificial weathering conditions equivalent to intermittent rains totaling 39 in. per year, the waste effluents had pH values between 7.3 and 7.6 for nearly 4 months. In addition the trace element releases were reduced by 40 to 99-plus %. Figure 1 shows the effectiveness of this treatment in controlling trace element releases from this waste. Cost analyses carried out in 1978 show that sequential lime/limestone slurry treatment would cost between 22 and 50¢ per ton of cleaned coal (1978 dollars), which is competitive with the technologies already in use.

Although the lime/limestone slurry treatment has provided some very encouraging results, it lasts for only about 4 months under the conditions of the laboratory weathering tests. In fact, because the amount of limestone added is chemically equivalent to only about 10% of the pyrite in the waste, this treatment cannot be permanent unless oxidation of the waste is somehow prevented. However, we believe this treatment of the waste, followed by disposal in an anaerobic environment, would be useful as a comprehensive waste disposal strategy. The lime/limestone treatment would neutralize the acid initially present in the waste and control the trace element releases until the permanent anaerobic disposal could be implemented.

Some uncertainties remain concerning the lime/limestone treatment. Because this treatment has been evaluated with only one coal waste, we must determine if the observed performance is a general phenomenon or if it is unique to the material we tested. In addition, no attempt was made to optimize the treatment parameters. The effects of compaction of the waste pile or freeze/thaw cycles have not been studied. Finally, the mechanism by

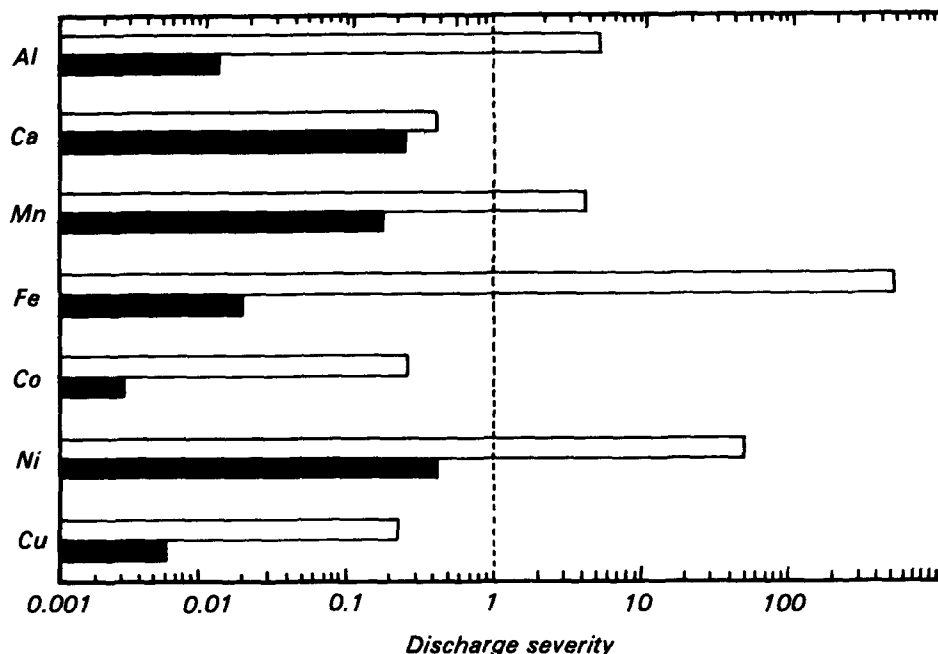


Figure 1. Discharge severities (leachate concentration/100 x Minimum Acute Toxicity Effluent/MATE) for selected trace elements in drainages from high sulfur coal preparation wastes - untreated wastes (unshaded) and lime/limestone treated wastes (shaded).

which this process works is only partially understood. All of these questions warrant study and will be addressed in the coming year.

Another way to neutralize acid *in situ* in coal wastes is to mix the refuse with alkaline soils or mine overburdens either before or during deposition in the waste dump. Alkaline process wastes, such as fly ash, could also be used. This possibility is attractive because it would be easy to implement and the required materials are inexpensive and readily available. Laboratory studies conducted this year with a variety of soils and process wastes show that alkaline materials are partly effective in controlling effluent quality when mixed with the coal waste or placed downstream of the waste. Concentrations of Al, Ni, F, and As (and the acidity) were all lower in the leachates for samples treated with the alkaline materials. Furthermore, the concentration decreases coincided with the increases in pH. However, the concentrations of Mn and Fe were higher in the leachates from the treated samples, probably because these elements were leached from the codisposed materials themselves. None of the materials tested could produce acceptable leachates during the initial leaching of the sample.

The same was true after regeneration of the waste pile by the passage of air through the waste. Therefore, codisposal of coal waste with these types of materials, at least by itself, is not likely to constitute a workable control technology. However, information gained from these studies will be useful in evaluating the effects of the mineralogy and underlying structure of potential disposal sites on the waste effluents. We are continuing these investigations to determine which soils or underburdens are most beneficial and which are most harmful to effluent quality.

The most widely used control technology for coal waste effluents is collection of the acidic drainages coupled with water treatment, usually alkaline neutralization. This approach is simple and uses proven technology. Also, cost analyses carried out in 1978 showed that this approach typically costs between 7 and 55¢ per ton of cleaned coal, so it is also relatively inexpensive. The obvious disadvantage is that water treatment must be continued as long as the waste pile retains any acid-generating potential, which can be hundreds of years. Nevertheless, because this technique is so widely used, and because its principle, alkaline neu-

tralization, is the same as that behind the best control technologies so far devised, additional investigation is warranted.

To study the chemistry of the neutralization process, we titrated a coal waste leachate with calcium hydroxide to various pH values and determined the concentrations of the trace elements left in solution. We then calculated the expected concentrations using a complex equilibrium code. The calculated and experimental values compare well for the major cations [calcium, aluminum, Fe(II) and Fe(III)]. However, the behaviors of the anions of major interest (sulfate, arsenate, borate, and fluoride) are not well accounted for in the thermodynamic model, except for fluoride. In addition, the important trace element concentrations are all lower than the calculated values. We speculate that these elements (As, Cd, Co, Cr, Cu, Mn, Ni, and Zn) are adsorbed on the hydrated iron and aluminum hydroxide precipitates. This behavior suggests that alkaline neutralization of coal waste leachates may actually be more effective in controlling the release of trace metal cations than thermodynamic calculations predict. Although these theoretical calculations cannot yet describe such complex chemical systems, they are valuable in identifying the factors controlling the solubilities of potential pollutants. Therefore, we will continue this line of investigation next year.

The formation of acid in the coal waste can be prevented in two ways. One is to dispose of the waste in an anaerobic environment (nonoxidizing) so that the pyrite cannot oxidize. This is essentially a return of the coal waste to the type of environment from which it originally came. Disposal of the waste in this way is simple in principle, and once the anaerobic conditions are established, no further treatment is required to control the waste effluents as long as the disposal site is not disturbed. However, it takes a significant length of time to properly structure such a disposal site, and during this time, the acid generated in the pile must be controlled. We believe that combining anaerobic disposal with a short-term method, such as the lime/limestone treatment, offers an acceptable solution to coal waste disposal.

The second way to prevent acid generation is to destroy the pyrite so that, even under oxidizing conditions, the waste has no acid-generating capability

In past studies we have shown that calcining, which destroys pyrite, is effective in controlling the leachabilities of the trace elements in high-sulfur coal wastes from the Illinois Basin. Calcining is a one-time permanent treatment. Thus, the treated materials can be disposed of conventionally without concern for their potential behavior in the distant and unforeseeable future. However, calcining merely exchanges one problem for another. The coal wastes are rendered innocuous because calcining drives off the sulfur, which eliminates the acid-generating capacity of the waste. The solids are left inert, but the evolved sulfur must be dealt with, either by flue gas desulfurization or by some technique of retaining the sulfur in the solid waste. Also, costs are high—not only for the control of the evolved sulfur, but also for the energy required to heat the mineral matter to the required temperatures. In fact, our cost studies show that the cost of calcining coal wastes can be as high as \$10.00 per ton of cleaned coal (March 1978), clearly placing this technology beyond the realm of economic feasibility. Nevertheless, we recently conducted some experiments to determine if waste from Plant K calcines in the same manner as that from Plant B. We found that trace releases from Plant K mineral wastes, when calcined at the optimum conditions for Plant B, are not as well controlled. The discharge severities for Mn and Ni remained larger than unity after calcining, and significant discharge severities ($0.1 < DS < 1.0$) were observed for Al, Cu, and Fe. These results were quite unexpected in view of the similarity of the mineral makeup of the wastes. Conditions may have not been optimum for these wastes, or other factors may be involved, but we have not initiated the experimental program required to determine the reasons. We believe that, because the treatment is very expensive, additional intensive study is unwarranted.

Assessment of High-Sulfur Appalachian Coal Wastes.

During the past year we have systematically studied the refuse from two coal cleaning plants in western Pennsylvania. These plants, Plants I and K, process high-sulfur Appalachian coal, although they use different processes. The laboratory work has been completed for both plants, but because the data are

complete only for Plant K, the results for Plant K are presented in this report; results for Plant I will be presented in the next annual report. Plant K is a jig operation and is unusual among the plants we have studied because the fines are not cleaned, but are sent straight through the plant and combined with the clean coal. Consequently, the plant output consists of cleaned coal, coarse mineral matter, and a 60-mesh slurry effluent. In this study, we have examined only the coarse refuse, the cleaned coal, and the raw feed coal.

In general, the mineral content of the waste from Plant K is comparable to that previously studied from the Illinois Basin. The Plant K material has a slightly lower sulfur content, but slightly higher concentrations of Li, Cl, As, Cd, Sb, and Lu. Except for Zn and Rb, which are slightly lower in the Plant K waste, all the remaining elements are present in comparable concentrations. No marcasite was detected, but the pyrite concentrations (~25%) are typical of the high-sulfur coal wastes of siderite (FeCO_3). This is the first time we have found this mineral in coal wastes. The Ca content of the Plant K refuse is low, which suggests that little or no calcite is present. This material has little or no self-neutralizing capacity.

Before chemical and mineralogical analyses, the refuse from Plant K was separated into seven fractions, based on the gross external appearances of the various pieces. Examination of these fractions along with the composite waste permitted us to derive some very useful information about the relationships between some of the trace elements and the various mineral phases. Most of the leachable trace elements tend to concentrate in those fractions containing the highest concentrations of clays and other silicate minerals. However, certain elements (Se, As, Sb, Cd, and Fe) are associated with the pyritic minerals. These elements are undoubtedly present in the form of sulfides (or selenide) and some of them are important because of their toxicological properties. Leaching studies (described below) suggest that the chemistry of these elements in the waste pile effluents is somewhat different than that of the rest of the trace elements.

We performed micromineralogical studies of these coal wastes, using electron microscopy coupled with energy dispersive spectrometry. Because this technique observes such a small

fraction of the sample at any one time, the results must be interpreted carefully. Nevertheless, one can perform elemental analyses while retaining the spatial resolution of the microscope. This is difficult, if not impossible, with other techniques. These studies confirmed our observations that most of the trace elements are associated with various types of clays. In addition, the trace elements seem to be present as discrete mineral phases, rather than in chemical associations with the gross minerals.

We performed static leaching experiments in which the coal waste was shaken with deionized water for from 1 to 50 days. The mixtures were then filtered, and the filtrate was analyzed for acidity, specific conductance, and trace element content. All these measurements increased with leaching time. Often, the leachates were very acidic, with pH values less than 2, indicating that this waste could generate drainages of environmental concern. Fe, As, Ni, Mn, and Al had discharge severities greater than unity, indicating sufficient concentrations in the waste effluents to be of environmental concern. Zn, Cd, and Cu had discharge severities between 0.5 and 1.0, suggesting that these elements may be cause for concern under certain circumstances.

The concentrations of several trace elements increase sharply with increased time, and they continue to increase even after most of the other elemental concentrations have reached steady-state values. These elements, As, Se, and Cd, are associated with sulfide mineral phases, possibly as sulfides (or selenide). We surmise that the mobilization of these elements depends not only on the pH of the leachate, but also on the rate at which the respective mineral phases are oxidized.

In addition to the static leaching experiments, we also performed a series of dynamic leaching experiments with the coal wastes by placing the coal waste into glass columns and pumping deionized water through the columns at a slow and constant rate. The effluents from the columns were sampled and analyzed periodically for acidity, specific conductance, and trace element concentrations. After all these values had reached steady state, the leachate flows were stopped for 2 weeks and air was forced through the columns. The leachate flows were then resumed and the experiment continued as before until

the trace element concentrations in the effluents again reached steady state. This experiment is designed to simulate the weathering of an uncontrolled waste pile that is intermittently exposed to wet (rain) and dry cycles. The initial leachates are very acidic when they emerge from the waste column, with pH values from 1.9 to 2.2. As the leachate flow continues, these decay to more moderate values (~4). After the columns are "regenerated" by passing air through them, the initial pH values are again very low (~2.3-2.4). Continuation of the leachate flow also causes these values to decay to moderate steady-state values (~4). Trace element concentrations behave in exactly the same way as the solution acidity (Figure 2). This behavior can be explained. Before the experiment the coal waste is exposed to air in the normal course of handling and sample preparation. This causes some oxidation to take place. The oxidation of pyrite in the waste leads to the formation of sulfuric acid, which accumulates in the waste until it is washed out by the leachate early in the leaching experiment. As the leaching proceeds, both the acidity and the trace element concentrations decay to more moderate steady-state values. However, when the leachate flow is interrupted and air is forced through the column, oxidation again takes place and the resulting acid accumulates in the waste until leaching is resumed. Thus when water is again allowed to flow through the column, the

initial effluents are very acidic and the trace element concentrations are very high. Our observations of very acidic leachates after air regeneration of the waste column suggest that this waste has strong acid-generating tendencies, and that the acid-drainage problem associated with this waste, significant even under steady-state conditions, is aggravated when the leaching is intermittent.

The initial discharge severities of Fe, Ni, and Mn were all greater than unity, but Fe, with a discharge severity of more than 100, was by far the worst offender. In addition, Zn, Cd, Al, and Cu had initial discharge severities between 0.5 and 1.0. These elements may pose problems of environmental concern under certain weathering conditions. In past reports in this series, we showed that trace element concentrations in the leachates are controlled by the pH. However, in certain cases (Pb, As, and possibly Co and Al), other factors are involved. The most important of these is probably oxidation of the minerals containing these elements.

In summary, the experimental evidence seems to indicate that the high-sulfur waste from Plant K may pose problems with serious environmental consequences unless it is properly disposed of. These problems are caused by the high acidities and the high concentrations of several trace elements in the waste effluents. Although our laboratory leaching conditions may be somewhat

more severe than those encountered in a large waste pile, it is clear from our field work that there is cause for concern in the disposal of these solid wastes. The behaviors of these materials exactly parallel those of the high-sulfur wastes from the Illinois Basin. While there is every reason to believe that the same control technologies will work for each of these coal wastes, we plan to test some of the more promising techniques with this waste as well as that from plants in the Illinois Basin.

Leaching Procedures

Throughout our investigation of coal waste, we have attempted to devise leaching tests that provide meaningful information on the environmental behavior of these materials. Accordingly, we have developed several procedures and have used the results of these tests as the basis for our predictions on the weathering behaviors of coal cleaning wastes. However there remains the question of how these procedures compare with those used by other researchers and, in particular, how they relate to the EPA extraction procedure used to classify wastes under the Resource Conservation and Recovery Act (RCRA). We addressed this question by comparing the results of our leaching procedures to those obtained using the EPA extraction procedure.

Seven mineral wastes from coal preparation plants in the Illinois Basin, Appalachia, and the western U.S. were leached in accordance with the EPA extraction procedure published in the Federal Register of May 19, 1980. This amounts to using 100 g of waste, ground to pass through a 9.3-mm standard sieve (-3/8 in.), adding 1600 ml of deionized water to the waste, and agitating for 24 h in an extractor designed to ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. The pH values of the mixtures are monitored during the extraction and, if the pH is greater than 5, adjustment must be made by adding 0.5N acetic acid. After 24 h, the solids are removed by filtration, and the concentrations of eight elements (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se) in the filtrate are determined.

The primary differences between our leaching procedures and that prescribed by EPA are the use of a higher liquid-to-solids ratio in the EPA test, the examination of a different set of elements by the EPA test, and the requirement that

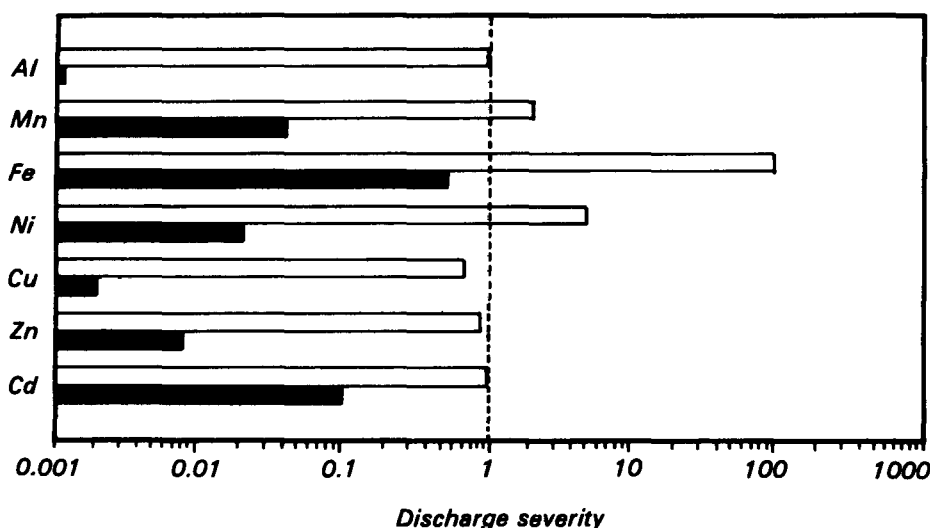


Figure 2. Discharge severities (leachate concentration/100 x MATE) for selected trace elements in leachates from Plant K coal preparation wastes as determined by dynamic leaching experiments—initial (unshaded) and steady-state (shaded).

alkaline systems be acidified in the EPA procedure. Compared to leaching tests that we have used over the past several years in our research on coal wastes, the results of the EPA procedure compare favorably with those of our procedures for elements examined by both.

Among the samples that we leached according to the EPA procedure, only the western coal waste required addition of acetic acid to maintain the pH below 5. Judged according to the criteria in the Federal Register, all the coal waste leachates had trace element concentrations below the maximum values set by EPA.

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The complete report, entitled "Trace Element Characterization of Coal Wastes—Fifth Annual Progress Report," (Order No. PB 82-219 379; Cost: \$12.00, subject to change) will be available only from:

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