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BIOGEOCHEMISTRY OF URANIUM MILL WASTES

Program Overview and Conclusions

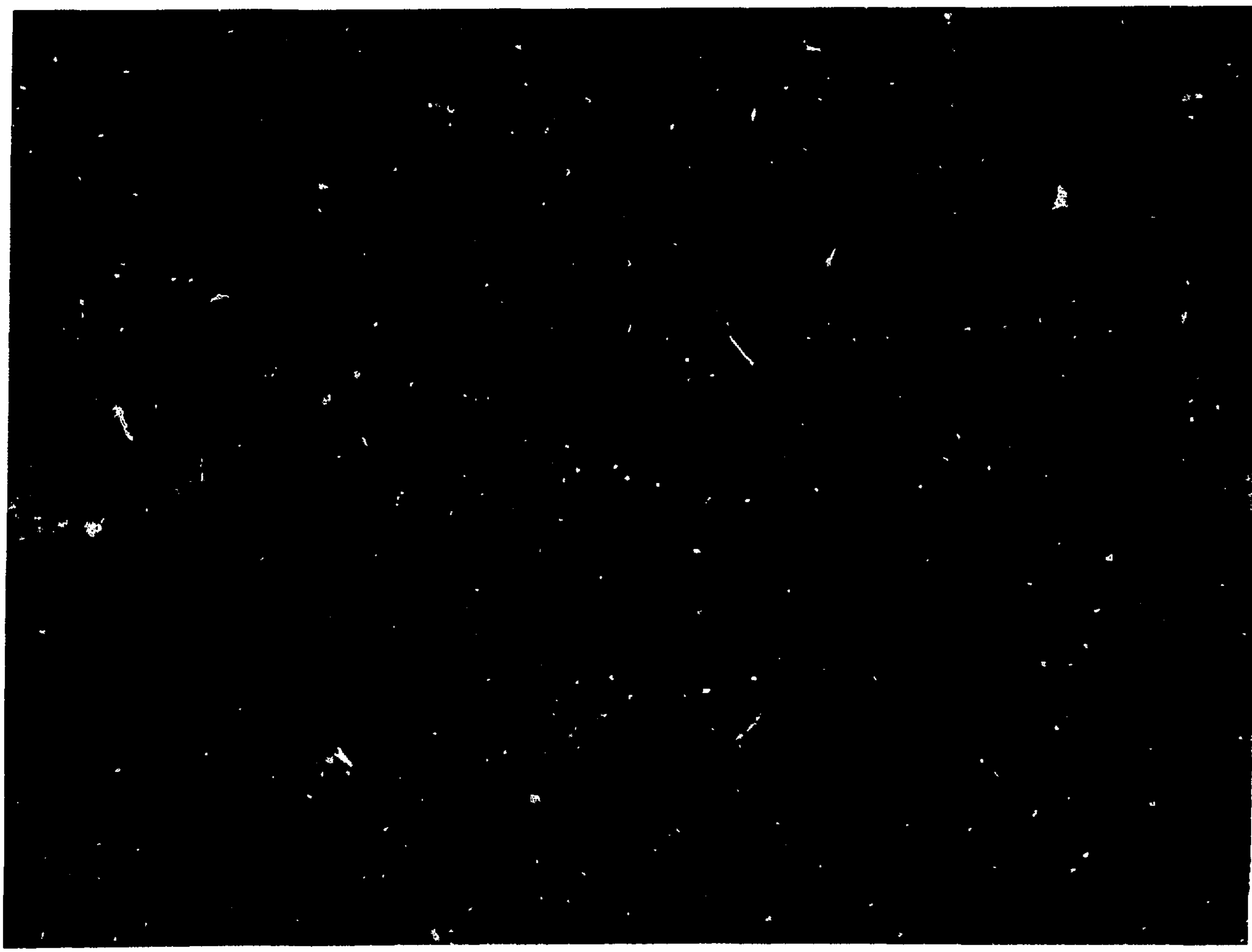

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Figure 1. Tailings sites in the Western United States.

a Monument Valley, Arizona; tailings piles in foreground.

b Monticello, Utah. Revegetated tailings piles on both sides of South Creek; riprap to prevent erosion.

c Milan, New Mexico. Inactive tailings pile in foreground, active tailings pile in background.

d Ambrosia Lake, New Mexico. Tailings pile with intermittent pond collecting surface runoff; inactive mill in midground.

e Slick Rock, Colorado. Tailings area sloping toward the Dolores River.

f Rifle, Colorado. Revegetated tailings areas established with sprinkler irrigation.

Cover

Typical of the geology and vegetation in arid regions of the Colorado Plateau where much of the uranium resource occurs. This location is near the Monument Valley tailings pile.

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ABSTRACT

The major findings and conclusions are summarized for research on uranium mill tailings for the US Department of Energy and the US Nuclear Regulatory Commission. An overview of results and interpretations is presented for investigations of ^{222}Rn emissions, revegetation of tailings and mine spoils, and trace element enrichment, mobility, and bioavailability. A brief discussion addresses the implications of these findings in relation to tailings disposal technology and proposed uranium recovery processes.

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BIOGEOCHEMISTRY OF URANIUM MILL WASTES PROGRAM OVERVIEW AND CONCLUSIONS

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This overview statement summarizes the major findings and conclusions produced by the Biogeochemistry of Uranium Mill Wastes research program, which is being conducted at the Los Alamos National Laboratory, under contract to the US Department of Energy. Results of an adjunct research program for the US Nuclear Regulatory Commission are also discussed regarding the environmental implications of the disposal of uranium mill tailings.

The Laboratory uranium mill tailings research program was initiated in July 1975 to investigate revegetation as a means of stabilizing 21 inactive uranium mill tailings piles in the Western United States. A preliminary survey of several inactive sites located in a wide variety of environments (Figs. 1a through f), and a review of the available literature showed that revegetation of these tailings disposal sites would not control the release of hazardous substances. In addition, it became evident that, without intensive irrigation and application of soil amendments, establishing vegetation in arid to semiarid regions on hostile tailings material is impractical.

Potential environmental degradation resulting from the dispersal of toxic trace elements present in tailings had received little attention by the various state and federal agencies responsible for regulating the uranium mining and milling industry. This aspect of tailings disposal gradually became the paramount focus of our studies; thus, our objectives were modified to assess the potential trace element releases from inactive tailings piles and to determine how these transport pathways may influence the technology of long-term stabilization of mill tailings.

I. EARLY FIELD STUDIES

The early stages of this program investigated ^{222}Rn flux from inactive tailings, the attenuation of this flux by soil covers, the feasibility of establishing native vegetation on bare and soil-covered tailings, and the revegetation of open-pit uranium mine overburden material.

A. Radon-222 Flux

- Radon flux from inactive tailings was temporally quite variable. At one location on an inactive alkaline tailings pile, flux measurements varied from 290 to 1740 atoms/cm^2/s with a mean of 940 and a standard deviation of 290 for 16 measurements taken over 14 months.[1,2]

- Mean radon fluxes varied appreciably among locations on the same tailings pile (i.e., means ranged from 500 to 1200 atoms/cm^2/s) as a result of differences in ^{226}Ra content, thickness of tailings, tailings texture, and variable moisture retention.[1,2]

Conclusion. Radon-222 source terms or average exhalation rates are not easily quantified if appreciable confidence is required in these parameters. Initial radon flux will be difficult to establish precisely, but such data are necessary if standards for control include a certain percentage reduction in flux.

B. Attenuation of Radon-222 Flux by Soil Covers

- Covers of clay soil 30 to 40 cm thick reduced radon flux an average of 30%, which agrees fairly well with predictions derived from a one-dimensional, two-layer, diffusion model However, the per cent attenuation varied from 3 to 73% with these covers for individual locations and times, indicating the large influence on flux reduction by atmospheric and substrate conditions.[1,2]

- One-meter-thick soil covers at two tailings sites provided mean flux reductions (± one std dev) of 57 ± 36% and 89 ± 9%. However, at one location, only 6% reduction was found, probably as a result of wind-deposited tailings or uranium ore dust on the surface of the soil cover. Theoretical predictions indicate that a 1-m clay soil cover should reduce radon flux by 80% .[1]

Conclusion A consistent attenuation of radon flux requires uniformity of soil thickness, soil texture, moisture content of the soil cover, and degree of compaction.

Compliance with radon flux attenuation standards would be quite difficult to establish on the basis of measurements. These difficulties have caused some regulatory agencies to set radon attenuation criteria on the basis of a *calculated* flux reduction. Fugitive tailings or ore dusts deposited on stabilized (covered) tailings areas can negate much of the desired flux reduction.

C. Establishing Native Vegetation on Tailings

- At best, marginal success was achieved in establishing native plant species (grasses and shrubs), without irrigation, on bare tailings or on shallow-soil-covered tailings in these semiarid environments. The tailings surface is a hostile environment for the germination and establishment of plant seedlings (Fig. 2a,b,e) because of high salinity, extremes in pH, the presence of toxic constituents, severe desiccation of the substrate surface, and wind blast damage to seedlings from windborne tailings sands. Soil covers alleviate the hostile chemical environment temporarily, but do not ameliorate the severe desiccating environment.[1,3]

- A layer of sandstone rock and boulders placed on the tailings surface resulted in the best establishment of native plants. This treatment caused the deposition of eolian tailings sands, which formed a favorable seedbed (Fig. 2f). The rock protected the seedlings from wind blast, conserved moisture, provided shade, and collected wind-blown seeds.[1,3]

- Vegetation samples were collected from many inactive tailings piles (Figs. 1b-f) in the Southwestern United States, some of which had been irrigated and/or covered with 20 to 50 cm of soil. Many of these samples had concentrations of As, Se, and ^{226}Ra that were appreciably above background concentrations. These elevated contaminant levels in the aboveground plant parts resulted from the uptake and translocation of contaminants and/or the contamination of the plant surfaces by wind-blown tailings.[1,3,4]

Conclusion. The establishment of dense vegetation on bare tailings in these semiarid environments requires intensive irrigation. However, irrigation may result in the leaching of contaminants into surface or groundwaters. The fate of a vegetation community upon cessation of irrigation may be the loss of most, if not all, of the established vegetation. Using rock riprap to encourage vegetation establishment without irrigation may be a more feasible and desirable approach in the semiarid Western United States. In addition, plants grown on bare tailings with irrigation or in shallow soil covers appear to assimilate toxic trace elements and radionuclides from the tailings.

D. Revegetation of Uranium Mine Overburden

- Overburden material from an open-pit uranium mine was successfully revegetated by segregating material from a particular geologic stratum to cover the surface of the overburden dumps (see Figs. 3a-f). This geologic material, when crushed and fertilized, provided a seedbed favorable to native plant establishment because of low salinity, favorable pH, lack of available toxic elements, and a fairly coarse texture, which provided good infiltration and retention of soil moisture.[3]

Conclusion. Some overburden strata, if segregated, may provide a more favorable substrate for revegetation than local topsoil.

II. TRACE ELEMENT MOBILITY AND BIOAVAILABILITY

The more recent objectives of this program concentrate on evaluating contamination of biotic and abiotic ecosystem components. This may result from the release of trace elements enriched in uranium ores and mill tailings. These studies have been directed at those elements enriched in tailings, their mobilization by aqueous media, their movement in groundwater away from tailings disposal sites, and their assimilation by plants.

A. Trace Element Enrichment

- Geologists and geochemists have determined that Mo, Se, As, and V are often enriched in sandstone uranium ores and in the surrounding low-grade or barren material. A widely accepted explanation for this enrichment is that these elements are present as oxyanions or anion complexes (e.g., uranyl tricarbonate) in oxidative groundwaters. These groundwaters move through porous sedimentary formations and encounter reducing zones; the reducing conditions are found in the presence of precipitated humic substances and H_2S. In the reducing zone deposition of these elements occurs. Some sandstone ore zones can contain elevated concentrations of heavy metals such as Pb, Cu, Ni, Co, and Zn, which are often associated with pyrites; however, these elements are not ubiquitous in sandstone uranium ores and their deposition is not analogous to that of uranium (see literature cited in Ref. 1).

- Tailings representing several mining districts in the Southwestern United States have been analyzed for trace element content. An alkaline tailings material from New Mexico was enriched relative to local surface soils by factors of 73 for Mo, 70 for U, 33 for Se, 28 for V, and 7 for As. Tailings from a salt roast, carbonate leach process in Colorado were enriched by factors of 112 for U, 48 for V, 10 for Se, 10 for Mo, and 8 for As, compared with typical soils. In general, mean ^{226}Ra activity ranges from 500 to 1000 times background for tailings from inactive mill sites that processed fairly high grade ore (~0.2 to 0.4% U). Concentrations of these enriched trace elements are usually higher in the finer tailings (slimes) than in the sands because these elements are often associated with clays and colloidal organic material. An interlaboratory analytical comparison of As, Mo, and Se in uranium mill tailings water demonstrated the difficulty of obtaining reliable analyses of these elements in complex environmental matrices.[1,5,6]

Conclusion. A characteristic group of trace elements is often enriched in sandstone uranium ores. Their deposition probably resulted from reducing conditions. The mining and, to a greater extent, the milling promote oxidizing conditions and thus the mobility of these elements may likely be reestablished.

B. Aqueous Mobilization of Trace Elements in Tailings

- The mobility of trace elements enriched in an alkaline tailings material has been evaluated using leaching (extraction) tests. Distilled water extracted 59% of the Mo, 42% of the Se, 13% of the As, 11% of the U, and 0.7% of the V present in the tailings material. The elements in the tailings extract were compared with soil extract concentrations for several surface soils. The factors for enrichment in the tailings extract vs the mean soil extract were 410 for U, 196 for Se, 81 for Mo, 31 for As, and 27 for V. Extract enrichment factors for a tailings material representing a different mill process and type of ore were 131 for U and 125 for V, with the other elements less than 10 times as concentrated in the tailings extract vs the soil extracts.

Conclusion. The trace elements associated with sandstone uranium deposits can be leached from tailings materials by aqueous solutions (Fig. 2c). The type of ore mineralization and the milling process influence the degree of mobilization of these elements.

C. Groundwater Transport of Trace Elements

- Monitoring wells were placed in shallow groundwater beneath and adjacent to an inactive alkaline tailings pile to provide samples for groundwater quality assessment. Groundwater hydrologically upgradient from the tailings pile contained 0.2 to 2.4 mg/ℓ Mo, 0.1 to 3.3 mg/ℓ U, and 50 to 680 mg/ℓ Na. Downgradient groundwater contained 29 to 52 mg/ℓ Mo, 4.6 to 8.1 mg/ℓ U, and 1200 to 2300 mg/ℓ Na. Waters within and beneath the tailings pile contained up to 333 mg/ℓ Mo, 12.3 mg/ℓ U, and 4800 mg/ℓ Na.[1]

Conclusion. The chemical data on these groundwaters, combined with knowledge of the hydrogeologic regime near this tailings disposal site (Fig. 2d), strongly indicate that these tailings are responsible for the contamination of shallow groundwater downgradient from the pile.

- Groundwater samples have been collected in the vicinity of an operating alkaline leach uranium mill in Colorado to provide a confirming evaluation for the US Nuclear Regulatory Commission. Contaminated shallow groundwaters more than 2 km from the tailings ponds have been used to supply irrigation for small fields and garden plots. One groundwater that was used in the past for irrigating crops contained 2.2 mg/ℓ U, 24 mg/ℓ Mo, 2400 mg/ℓ SO_4, and 120 mg/ℓ Cl. Other uncontaminated groundwater samples collected at a distance from the mill contained only 0.02 mg/ℓ U, 0.02 mg/ℓ Mo, 60 mg/ℓ SO_4, and 10 mg/ℓ Cl.

Conclusion. The groundwater flow patterns near this uranium mill are not well established. However, existing evidence indicates that the most probable source of contaminated groundwater is seepage from the mill tailings ponds because groundwater within the mill property boundaries shows high levels of these contaminants. No other industrial activity or natural source has yet been found to explain this groundwater contamination. Although natural groundwaters in the area vary in quality, several residential (irrigation) wells with abnormally high levels of these contaminants can be identified. The transport of these contaminants (presumed to be present as anions) appears to have occurred over a large distance (>2 km), and again illustrates their potential mobility.

D. Uptake of Tailings Contaminants by Plants

- In addition to the groundwaters discussed earlier, soil and vegetation samples were collected in the vicinity of this operating mill in Colorado. Particular attention was given to those samples from fields irrigated with contaminated groundwater. Significantly elevated levels of U, 10 µg/g, and Mo, 14 µg/g, were found in soils irrigated with the contaminated groundwater mentioned in Sec. II.C. These concentrations can be compared with mean background levels of 4 µg/g U and 3.6 µg/g Mo. Grasses grown in these contaminated soils have a U content that ranges from 0.6 to 2.0 µg/g (dry weight basis), compared with grass from background locations containing 0.1 to 0.3 μg/g. Molybdenum levels in grass range from 29 to 187 μg/g from this contaminated site vs background grass concentrations of <1 to 5 μg/g. Copper-to-molybdenum ratios range from 0.4 to 1.6 compared with background ratios of 6.7 to 78.

Conclusion. The application of irrigation water contaminated with appreciable levels of Mo and U can result in the accumulation of these contaminants in soils and can cause significantly elevated levels of these trace elements in vegetation. The Mo levels in vegetation from the impacted site and the resultant low Cu-to-Mo ratios (i.e., Cu/Mo < 2) have been cited by other researchers as posing a threat of molybdenosis to grazing animals (particularly cattle and sheep) consuming substantial amounts of this forage. Some 15 years ago, cattle with symptoms of molybdenosis were observed in these fields irrigated with contaminated groundwater.

- Greenhouse experiments were performed to better identify those tailings contaminants assimilated by plants and translocated to the aboveground plant parts. Two native plant species, a grass and a shrub, were grown in pots containing alkaline tailings with covers of local soils. Molybdenum and selenium were enriched to levels up to 72 and 35 times, respectively, the levels found in vegetation grown in the soil controls. The activity of ^{226}Ra in plants grown in tailings was up to 27 times the level found in plants grown in soil. In addition, for the shrub species, U was up to 300 times more concentrated in plants from tailings treatments vs controls; the grass species had only 2 to 3 times more U when grown in tailings. The levels of Mo and Se in these species grown in tailings were well above levels reported to cause toxicities to grazing animals.[4,7]

Conclusion. A definite hazard to higher trophic levels in the food chain exists if plant roots are allowed to penetrate into tailings material. The degree of hazard depends on the plant species and the bioavailability of contaminants in the tailings material.

III. DISCUSSION, INTERPRETATION, AND RECOMMENDATIONS

A. Trace element contamination of the environment from tailings piles stabilized with soil covers may be a problem because of seepage of mobile contaminants into groundwater or penetration of plant roots through soil covers into tailings. These mechanisms may also be capable of transporting radionuclides into the environment.

- The most prevalent proposed solution to seepage is the use of synthetic film or clay liners, but degradation in this harsh environment causes some uncertainty about the longevity of these liners. A promising scheme to control seepage involves the disposal of tailings as a moist solid after dewatering the tailings slurry using belt filtration. Removing most of the spent leach solution before disposal eliminates most of the transport media for contaminant movement. If such dewatered tailings are buried in trenches excavated in fairly impermeable geologic formations far above groundwater occurrences, the possibility of seepage and contaminant movement is severely limited. Other controls would not attempt to stop seepage, but would depend on the subsoil and deeper geologic strata to attenuate mobile contaminants. This approach would require a thorough knowledge of the attenuating capacity of soils and geologic material under and adjacent to a tailings disposal site.

- Prevention of plant root penetration into tailings may require one or more of the following barriers:

(a) A soil cover thicker than the anticipated plant root penetration depth,

(b) a long-term physical barrier to root penetration (possibly some type of polymeric film),

(c) a long-lived chemical barrier hostile to plant root growth (perhaps a layer of herbicide or a layer of salt producing high osmotic potential, which would reduce available soil water), or

(d) a barrier designed specifically to prevent moisture penetration and concomitant root penetration.

Another strategy, probably not feasible, is the long-term maintenance of shallow-rooted plant species on the stabilized tailings piles. Reducing the amount of available water beneath the cover by dewatering tailings might discourage deep root growth.

B. The US Nuclear Regulatory Commission and other federal and state regulatory agencies seem to consider ^{222}Rn emissions from tailings areas as the most critical contaminant pathway requiring rigorous control. At this time, the control technology most often proposed includes thick soil or clay covers over tailings to act as radon diffusion barriers. However, other researchers are evaluating more exotic radon barriers, such as asphalt emulsion sealants. The major question regarding the effectiveness of these radon diffusion barrriers is the permanence of the barriers. Wind and water erosion can remove soil covers;

physical and chemical degradation of polymeric or asphalt sealants may occur; plant roots or burrowing animals may disrupt these barriers. Thus, whether these barriers can actually reduce radon flux over the long term remains. It appears that the more conventional disposal and stabilization technologies for uranium mill tailings may, in fact, rely on natural atmospheric dispersion (dilution) of ^{222}Rn and progeny as the long-term mitigating factor.

C. A tailings management scenario that appears to be technologically and economically feasible at this time includes (a) dewatering tailings, (b) placement of tailings solids into trenches in impermeable geologic material (i.e., shale) or in clay-lined trenches, (c) disposal of tailings liquids by recycling as mill solutions, evaporation in clay-lined ponds, or treatment to remove contaminants before discharge, (d) placement of excavated material from adjacent trenches on top of tailings solids to provide cover depths of 5 to 10 m, and (e) compacting excavated material and covering with riprap.

D. Future milling technologies may provide the best solution to the dilemma of uranium mill tailings management. Laboratory scale studies by researchers in Canada and in the United States have shown promising results for removing trace element and radionuclide contaminants from tailings solids or ores by nitric acid leaching or by high temperature chlorination and hydrochloric acid leaching. If the bulk of the tailings solids can be made environmentally innocuous, disposal should be simple and the solids might be used for construction purposes. Mineral values, other than uranium, leached from ores should be recoverable and should offset some of the increased costs of such milling operations. The small volume of highly contaminated residues remaining could be transported to a facility committed to the disposal of such wastes. The possibility of disposing of an innocuous bulk residue is attractive compared with present tailings disposal alternatives.

E. *In situ* solution mining of sandstone uranium ores is receiving increased attention as an alternative to conventional mining and milling operations. The capability of recovering uranium without the disposal of tailings is worthy of consideration, but a major problem that has received little consideration is the possibility that the oxidizing leaching solution (lixiviant) pumped into the ore zones will oxidize minerals of As, Se, Mo, and V, as well as U. The solubility of these oxidized minerals may be quite high, causing contamination of the aquifer. Restoration of aquifers after *in situ* solution mining is being planned. However, restoration may not be feasible because of the long-term release of the soluble constituents, which may permanently contaminate the aquifers.

F. The major finding of this research program is the potential hazard to the environment from mobile trace elements enriched in uranium mill tailings. The mobility poses a threat to groundwater resources as a result of seepage from tailings impoundments. The bioavailability of some of these trace contaminants could result in toxicity to biota if these constituents escape from tailings disposal sites. These contaminants pose an appreciable hazard to terrestrial and aquatic ecosystems exposed to effluents or emissions from uranium mining and milling wastes.

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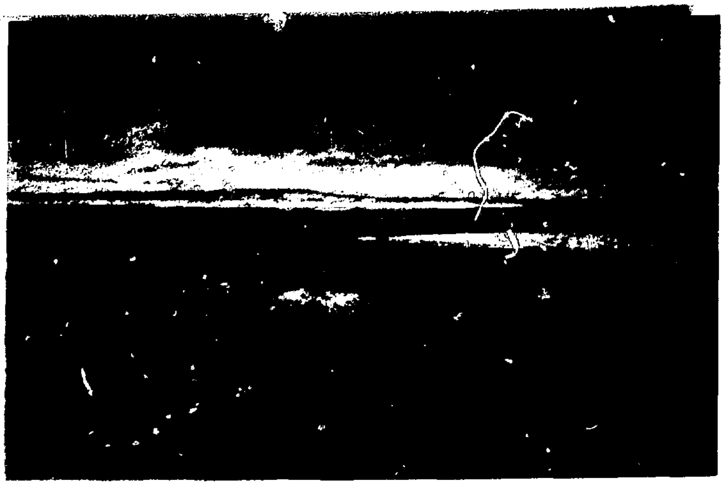

Figure 2. Transport mechanisms.

a *Tailings blowing off the Ambrosia Lake, New Mexico pile.*

b *Tailings sand dunes east (downwind) from the Ambrosia Lake pile.*

c *Tailings pond at the active mill at Bluewater, New Mexico.*

d *Storage pond for water pumped from underground uranium mines, Ambrosia Lake, New Mexico.*

e *Water erosion of tailings pile surface causing a dike breach, Ambrosia Lake, New Mexico.*

f *Perennial grass established in tailings sands accumulated between rock surface treatment used in revegetation studies.*

Figure 3. Uranium mine spoils revegetation.

a Open-pit uronium mine on the Laguna Indian Reservation in west central New Mexico.

b Mine spoils dump from open-pit mining operation.

c Top of mine spoils dump before crushing and grading.

d Mulching the graded surface of a dump.

e Early growth, after summer rains, of barley (from mulch) and native grasses.

f Native grasses, shrubs, and herbaceous species established without irrigation.