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Characterization of Soil Samples From the St. Louis, Missouri, FUSRAP Site

By C. L. Mardock and D. C. Dahlin

August 10, 1995

Report Prepared Through Interagency Agreement With the Department of Energy

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Department of the Interior
U. S. Bureau of Mines
Albany Research Center

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BUREAU OF MINES
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August 10, 1995

Mr. James G. Hart
U.S. Department of Energy
Former Sites Restoration Division
Oak Ridge Operations Office
200 Administration Road
P.O. Box 2001
Oak Ridge, TN 37831-8723

Dear Mr. Hart:

Enclosed are two copies of the characterization report, "Characterization of Soil Samples From the St. Louis, Missouri, FUSRAP Site" by C. L. Mardock and D. C. Dahlin, completed in response to your request for support (March 7, 1995) for the DOE FUSRAP activities at St. Louis, MO. The work was completed under Interagency Agreement DE-AI05-930R22161 between the Department of Energy and the U.S. Bureau of Mines. This report relates to the fourth task in that request:

> Task 4. Perform scanning-electron microscope examination on 25 mounts prepared from sized fractions of 6 composite soil samples from the St. Louis site.

Rust - Clemson Technical Center sent archived remainders of three sized but otherwise untreated splits from each of six requested composite samples. Heavy-liquid separations were performed on the two coarser size fractions. Grain mounts were prepared from the resulting heavy and light fractions and from the unseparated minus 38-μm size fractions. Consequently, 30 grain mounts were characterized instead of the 25 mounts called for in Task 4 at no extra cost.

As you requested, we have sent two copies of this report to Mr. Adler and two copies to Mr. Miller.

We appreciate the opportunity to provide our research results to DOE in support of the FUSRAP program. Please call me or Cheryl Mardock if you have any questions about our report.

Sincerely,

David C. Dahlin

David C. Dahlin
Metallurgist
Albany Research Center

Enclosures

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CHARACTERIZATION OF SOIL SAMPLES FROM THE ST. LOUIS, MISSOURI, FUSRAP SITE

by

C. L. Mardock and D. C. Dahlin

EXECUTIVE SUMMARY

The U S. Department of Energy (DOE) requested support from the U.S. Bureau of Mines Albany Research Center for DOE's investigation of radionuclide-contaminated soils at the Mallinckrodt and North County (St. Louis Airport) properties in St. Louis, Missouri, under the Formerly Utilized Sites Remedial Action Program (FUSRAP). This report describes the results of a mineralogical characterization study on size fractions from six composite soil samples from the North County properties.

The six soil samples had been previously sized into plus 150-µm, 150- by 38-µm, and minus 38-µm fractions. Heavy-liquid separation tests were done on the two coarser size fractions to aid in identification of the soil constituents. The heavy and light fractions from the heavy-liquid separation procedure and the unseparated minus 38-µm samples were prepared as polished grain mounts for scanning-electron microscope (SEM) studies.

Detailed mineralogical characterization studies were completed on 30 polished grain mounts with an Amray SEM equipped with a Kevex energy-dispersive x-ray (EDX) analyzer. In addition, nearly 6,000 high-atomic-weight grains and 1,000 medium- and low-atomic-weight grains in eight selected fractions were analyzed during automated scans and analyses for Th, U, and Ra on a Leica SEM equipped with an Oxford Link EDX system with light-element detection and with a Microspec wavelength-dispersive x-ray system.

The samples of soils examined in this study contain many mineral constituents that are typical of most soils. However, the heavy-mineral and process-product constituents that comprise 1 to 7 pct of these samples make the soils unique. The radioactive contamination consists primarily

of the isotopes of U, Th, and Ra, and is the result of processing uranium ores to recover U metal. The contamination takes the form of ore and other feedstocks, slags, residues, filter cakes, and precipitates; these heavy components contain almost all of the radioactive contamination in the samples. No contamination was attributed to the light-weight constituents, but low concentrations of radioactive elements could conceivably also be in these fractions.

The particle size distribution of the soils indicates that physical separation of contamination by physical mineral-processing methods is probably not a viable volume-reduction option. Screening would be ineffective, and gravity separation would be difficult, if possible at all.

Chemical extraction offers the best option to successfully reduce the level of contamination in these soils to acceptable levels, but process parameters must be optimized to overcome potential problems such as leachant penetration and solids/liquid separation. The results suggest that additional bench-scale tests would be appropriate to investigate this option.

INTRODUCTION

The U.S. Department of Energy (DOE) requested support from the U.S. Bureau of Mines Albany Research Center (ALRC) for DOE's investigation of radionuclide-contaminated soils at the Mallinckrodt and North County (St. Louis Airport) properties in St. Louis, Missouri, under the Formerly Utilized Sites Remedial Action Program (FUSRAP). The request was in the form of four tasks. Three tasks were reviews and evaluations of characterization and treatability studies about the properties, and these were completed by the Bureau in May 1995. The fourth task was a mineralogical characterization study on six soil samples from the North County properties:

> Task 4. Perform scanning-electron microscope examination on 25 mounts prepared from sized fractions of 6 composite soil samples from the St. Louis site.

This report describes the results of the Bureau's investigation in completion of task 4. RUST Federal Services - Clemson Technical Center (RUST-CTC) completed characterization

and extractability studies on both discrete and composited samples from the North County properties in January 1995 (Interim Characterization Report, 2 volumes). The RUST-CTC characterization studies consisted of particle size distribution, radioisotope distribution, bulk-density measurements, and preliminary chemical-extraction tests. The Bureau's mineralogical characterization study provides information about the nature of the radioactive contamination, how it occurs in the soils at the North County properties, and the implications for soil-treatability strategies.

DESCRIPTION OF SAMPLES

To better correlate the information from this investigation with information in the RUST-CTC report, it was agreed that RUST-CTC would send sized but otherwise untreated splits from six composite samples to ALRC for this study. A description of the samples is shown in table 1.

Table 1. Sample inventory.

	As-received		Heavy-liquid separation		
Sample no.	Size fraction	Weight, g	Fraction	Weight, pct	ALRC polished surface no.
BF1C	Plus 150 µm	36.1	Heavy	1.9	3252
			Light	98.1	3253
	150 by 38 µm	61.6	Heavy	2.4	3254
			Light	97.6	3255
	Minus 38 µm	3.1			3256
LV1C	Plus 150 µm	12.7	Heavy	0.5	3257
			Light	99.5	3258
	150 by 38 µm	40.5	Heavy	1.0	3259
			Light	99.0	3260
	Minus 38 µm	78.2			3261

Table 1. Sample inventory (cont'd).

	As-received		Heavy-liquid separation		
Sample no.	Size Fraction	Weight, g	Fraction	Weight, pct	ALRC polished surface no.
SL2C	Plus 150 µm	11.6	Heavy	2.9	3262
			Light	97.1	3263
	150 by 38 µm	34.6	Heavy	1.0	3264
			Light	99.0	3265
	Minus 38 µm	139.5			3266
BF3C	Plus 150 µm	1.4	Heavy	6.7	3267
			Light	93.3	3268
	150 by 38 µm	38.4	Heavy	1.9	3269
			Light	98.1	3270
	Minus 38 µm	105.8			3271
LV3C	Plus 150 µm	2.3	Heavy	4.2	3272
			Light	95.8	3273
	150 by 38 µm	38.5	Heavy	1.0	3274
			Light	99.0	3275
	Minus 38 µm	94.4			3276
SL3C	Plus 150 µm	3.0	Heavy	6.5	3277
			Light	93.5	3278
	150 by 38 µm	34.0	Heavy	1.8	3279
			Light	98.2	3280
	Minus 38 µm	66.8			3281

RUST-CTC identified the samples by location, activity group, and size. The samples are composites from three locations identified as Ball Field (BF), Latty Vicinity (LV), and St. Louis Airport (SL), and from three activity levels (low activity (1), intermediate activity (2), and high

activity (3)). The combination of sample locations and size fractions resulted in 30 rather than 25 polished surfaces for examination.

METHODS

The samples had been previously sized by RUST-CTC into plus 150-µm, 150- by 38-µm, and minus 38-µm fractions. At ALRC, each fraction was weighed and then prepared for further examination.

Heavy-liquid separation tests were done on the plus 150-µm and 150- by 38-µm size fractions to aid in identifying the constituents of the soils. The separation was accomplished using a solution of sodium polytungstate in distilled water at a specific gravity of 2.90 ± 0.02. Each as-received sample was mixed thoroughly on a rolling cloth and then progressively quartered to split approximately 5 grams of sample; if the sample weighed less than 5 grams, the entire sample was used. The sample was combined with the heavy liquid in a 50-ml plastic test tube, and the slurry was stirred to ensure complete wetting. The sample was centrifuged for 5 minutes at 1500 rpm, and then the test tube was dipped in liquid nitrogen to freeze the bottom portion of the heavy liquid that contained the heavy fraction. The light fraction was poured off from the frozen heavy fraction onto a vacuum filter and was thoroughly washed with distilled water. The heavy fraction was thawed and then filtered and washed the same way as the light fraction. The separated fractions were dried, and the recovered polytungstate solution was reused after appropriate adjustment of the specific gravity.

The heavy and light fractions from the heavy-liquid separation procedures and the unseparated minus 38-µm samples were prepared as polished grain mounts for scanning-electron microscope (SEM) studies. A representative portion of each sample was mounted in epoxy in a 1-inch-diameter mold. The mounted grains were then ground and polished on metallurgical grinding wheels with progressively finer grit to prepare a flat, polished surface for examination.

Detailed mineralogical characterization studies were completed with an Amray SEM equipped with a Kevex energy-dispersive x-ray (EDX) analyzer capable of detecting elements with atomic numbers greater than 10.[1] In addition, nearly 6,000 high-atomic-weight grains and 1,000 medium- and low-atomic-weight grains in eight selected samples were analyzed during automated scans and analyses for Th, U, and Ra on a Leica SEM equipped with an Oxford Link EDX system with light-element detection and with a Microspec wavelength-dispersive x-ray (WDX) system.

EDX and WDX analyses are based on the bombardment of a sample with a finely focused beam of electrons in the SEM. The beam strikes the surface of the sample and generates characteristic x-rays from the elements in the target area; analyses can be done on particles or areas as small as 1 μm in diameter. Computer-assisted examination and analysis of detector-collected x-rays in conjunction with backscattered-electron imaging allows identification of the constituent chemical elements. Concentration analyses are normalized based on the elements requested and may be quantitative or semi-quantitative, depending on analytical standards and the complexity of the sample matrix.

The EDX and WDX systems have a detection limit of approximately 3 pct for quantitative analysis and a detection limit approaching 1 pct for qualitative analysis; the minimum detection level depends upon the element. If an area of sample 1 μm or larger contains more than 1 to 3 pct of a high-atomic-number element, the SEM backscattered-electron image of that area will appear comparatively bright, and the EDX and WDX systems will detect the element. Interference from background radiation and from x-rays from overlapping or adjoining elements is a concern in these analyses, and sophisticated software is used to define quantities of overlapping elements. The definitive elemental spectra differ in EDX and WDX analysis, and both systems were used in this study to ascertain the presence of detectable radioactive elements.

[1]Reference to a specific brand name does not imply endorsement by the Bureau of Mines.

The grain mounts of the light fractions were also examined by reflected-light microscope for carbonaceous materials. Because carbon is used as a conductor coating on samples for SEM analysis, carbon in a sample is difficult to determine with an SEM.

RESULTS AND DISCUSSION

General Sample Description

The samples of soils from the North County properties examined in this study contain many mineral constituents that are typical of most soils. However, the heavy-mineral and process-product constituents that comprise 1 to 7 pct of these samples make the soils unique. The heavy minerals and process products are the components that contain most of the radioactive contamination in the samples, and thus are of most interest in this characterization study.

The radioactive contamination at the North County properties consists primarily of the isotopes of U, Th, and Ra, and is the result of processing uranium ores to recover U metal. The contamination takes the form of ore and other feedstocks, slags, residues, filter cakes, and precipitates. Because the fine size of the contaminated particles often precluded positive identification of the nature of the particles, the generic term, "process product," is used to distinguish these particles from nonradioactive natural minerals and other soil constituents.

Although no radioactive contamination was attributed to the light-weight constituents in these samples, low concentrations of radioactive elements, below the detection level of the SEM and EDX/WDX systems, could conceivably be present in these components of the soils. Isotopic analysis of these fractions was not part of this study, but they should be done to confirm this observation.

Radioactive and Suspected Radioactive Materials

The radioactive contamination characterized in this study is generally finer than the nonradioactive particles it is associated with, and it is predominantly associated with process products. Radioactive elements were identified in most of the Ba and Mg process products, and they are strongly suspected to be present in those products that showed no contamination based on EDX and WDX analyses. The contamination is rarely locked with, precipitated on, or otherwise associated with the natural soil constituents.

Uranium-bearing materials. Uranium, U oxides, and U-Pb compound particles are in Mg-F process products in most of the heavy fractions (figs. 1, 5, 8, 13, 18-20, 23, 31-32). Uranium oxides are reduced through a Mg-reduction process to produce U metal; the reaction is usually not complete, and slightly oxidized U particles often result. The uranium-bearing particles range in size from less than 1 to 50 µm in diameter and average 1 to 10 µm. The U particles are locked within Mg-F grains that range in size from 10 to 500 µm in diameter and average 50 to 300 µm. These Mg-F products also frequently contain one or more of the elements Si, Fe, Ca, Al, Cl, and Pb in concentrations up to 20 pct.

Some U occurs as small inclusions or concentrations (3 to 11 pct) in Ba process products. The U is often associated with Pb concentrations. The Ba products are combinations of unprocessed pitchblende ore, partially processed ore, and process products. The Ba products are usually complex compounds that contain up to 20 pct of one or more of the following additional elements: Ca, Fe, K, S, Si, Al, Sr, P, Cl, As, and/or Mn.

Some uranium is not associated with either Mg-F or Ba process products. Two 1- to 5-µm grains of U-U oxides were found in a fluorite grain, and two liberated 1- to 2-µm grains of U and U-Pb were also detected.

Thorium-bearing materials. Thorium is present primarily in discrete particles of monazite ($(Ce,La,Nd,Th)PO_4$). The Th concentration in the monazite ranges from 1 to 12 pct. Two small (5-µm), liberated particles of thorite ($ThSiO_4$) were also identified, as were traces of Th in zircon grains in the samples.

Thorium occurs naturally in pitchblende in concentrations from less than 1 pct to 14 pct, and it can be traced to the Ba process products in the samples. High concentrations of Th in small areas (10 to 20 μm) within the particles ranged from 14 to 17 pct.

Radium-bearing materials. Radium was not definitively identified in any of the samples. A near-detection-level Ra peak was recorded in a Ba process product by WDX analysis, and numerous near-background readings were recorded by EDX analysis, which is subject to more interference by other element signals than is WDX. However, no conclusive detectable Ra (greater than 3 pct) was identified in any of the samples. Qualitative activity measurements with a scintillometer on the mounted samples indicated that radioactive elements are present in the Ba and Mg-F process products in concentrations below the detection level of the SEM and EDX/WDX (less than 3 pct). Radium may substitute for Ba in the Ba products as a radiobarite ($(Ba,Ra)SO_4$). Radium may also be present in the Fe-Mn slag products, possibly associated with low concentrations of U, from the processing of pitchblende ore. Traces of Ra occur naturally in pitchblende and in monazite.

Natural Heavy Minerals.

The most abundant heavy natural minerals in the samples are undifferentiated minerals of the pyroxene and amphibole families. They comprise up to 50 pct of some heavy fractions but constitute less than 1 pct of the total sample. In the SEM photomicrographs that follow, these minerals are generally prismatic in form They are composed of various combinations of Ca, Fe, Mg, and Al silicates.

Iron and titanium minerals are the next most abundant in the heavy concentrates. The Fe minerals include magnetite, titaniferous magnetite, and goethite. They generally make up between 1 and 5 pct of the heavy fractions. Ti minerals include ilmenite, rutile, leucoxene, and sphene, and generally make up less than 1 pct of the heavy fractions.

Monazite and zircon comprise up 0.1 to 0.2 pct of the heavy fractions, both as liberated and locked particles. Both minerals are sources of Th and possibly Ra.

Trace amounts of other natural heavy minerals also occur in the samples. These include garnet, serpentine, chromite, pyrite, bastnasite, apatite, and gypsum. Only a few grains of these trace minerals were observed in the samples.

Barite is a natural mineral composition, but it is considered here to be a process product because $BaSO_4$ is a common residue of pitchblende processing.

Heavy Process Products

The heavy process products characterized in this study fall generally into four main categories: smooth pieces of Mg-F that often contain inclusions of U and Pb; frothy Ba process products that contain a wide variety of elemental compositions; mottled, glassy Fe slags, often rounded in shape, that contain Mn and other metals; and metals and oxides of Fe, Pb, and other metals. Intermediate chemical combinations of the Ba and Fe process products also occur.

The Mg-F process products often have inclusions of Pb and U. Other elements present in the Mg-F product in different concentrations up to 20 pct include Fe, Al, Si, and Cl. Particles of this process product, probably impure MgF_2 (specific gravity - 3.15), report consistently to the heavy fraction, regardless of the U and Pb content. This product ranges from 1 to as high as 40 pct of the heavy fractions.

The frothy Ba process products are often high in Ca and Pb, and can contain up to 20 pct of Fe, K, S, Si, Al, Sr, P, Cl, As, Mn, Ti, W, and U. These products make up from 1 to 20 pct of the heavy constituents.

The Fe-Mn slags contain different amounts of siliceous glass, and may contain Ti, Ca, Al, P, Mg, Pb, and, on rare occasions, Co, Ni, V, and Th. These slags comprise up to 5 pct of the

heavy fractions. Some of the more siliceous slags report to the light-weight fractions; this slag comprises more than 20 pct of one plus-150-µm, light-weight fraction.

Small amounts of metallic Fe and Pb are present in the samples. These metals rarely have additional elemental constituents but are often partially or wholly altered to oxides. Tramp metallic pieces of brass, solder, and stainless steel are present in trace amounts.

Light-Weight Natural Minerals

Liberated grains of quartz comprise up to 90 pct of the soil in the samples. In rare instances, these particles are locked with other minerals or rock fragments.

Feldspars make up the next most abundant natural mineral constituent in the samples and approach 15 pct in some of the samples. Several K-, Na-, and Ca-feldspars are present, many of which are actively altering to clays.

Calcite is the third most abundant natural light mineral in the samples. The calcite is present as mineral crystals and as limestone and shell fragments.

Clays, the result of alteration of the feldspars, make up the remainder of the natural light-weight constituents. Clay abundance increases in the finest size fraction.

Light-Weight Non-Mineral Soil Constituents

Wood and coal particles are numerous in many of the light-weight fractions, particularly in the plus 150-µm fractions. The wood is very porous, may exceed 1000 µm in length, and is relatively clean of other soil particles. Some of the coal has apatite and pyrite inclusions.

Siliceous Fe slags are present in most of the light-weight fractions. These slags may contain low-level radioactive concentrations, although none contained detectable levels in EDX and

WDX analyses.

Humus, colloidal oxides, and other natural non-mineral soil constituents comprise the remainder of the light-weight constituents. These particles, combined with clays and 1- to 5-µm grains of other constituents, may be responsible for durable filter-cake pieces prevalent in the minus 38-µm fractions.

Specific Sample Descriptions

The following sample descriptions are based on SEM examinations of polished mounts of light and heavy fractions of the plus 150-µm fractions and the 150- by 38-µm fractions and the minus 38-µm fractions of six composite soil samples.

The figures that accompany the sample descriptions are backscattered-electron images taken with the SEM. High average-atomic-number particles generate bright images, and the brightness decreases to darker shades of gray as the average atomic number of the particles decreases. For example, a concentration of a high-atomic-number radioactive element in a sample appears significantly brighter in a backscattered-electron image than silica or calcite, which are composed of low-atomic-number elements. However, in this set of figures, each photomicrograph was exposed at different settings of brightness and contrast to enhance the differences in the features of each image, and a bright species in one image may appear light gray or even dark gray in another image. Particle descriptions in the captions to the figures use the terms "bright" for the white to near-white particles, "medium" for mid-range gray particles, and "dark" for dark gray to near-black particles. The mounting epoxy appears black in all of the figures.

The photomicrographs show general low-magnification views of the radioactive species, the heavy-metal species, and low-specific-gravity species in the sample. Magnified images of individual grains are also shown to illustrate details of how the radioactive compounds occur.

BF1C plus 150-µm heavy fraction; polished section 3252. Heavy particles consist primarily of Fe, Fe oxides and Fe-Mn process products (fig. 1). Radioactive compounds in the sample include numerous small (1- to 10-µm) inclusions of U in a Mg-F process product and 50- to 100-µm particles of Pb with a trace of U in a siliceous Al-Si-Ca-P process product. Other heavy materials include pieces of Pb-Sn solder, a few minus 100-µm particles of a Ba process product, and a 500-µm piece of barite. Medium- and low-specific-gravity particles primarily include siliceous process products and traces of quartz and calcite.

BF1C plus 150-µm light fraction; polished section 3253. Light-weight materials are primarily calcite and quartz, with lesser amounts of siliceous process products, wood, coal, and other carbonaceous materials (fig. 2). Traces of heavy particles (Fe, Fe oxides, Fe process products, barite, garnet, and ilmenite) occur in this fraction. The natural minerals are often locked with quartz.

BF1C 150- by 38-µm heavy fraction; polished section 3254. The sample includes heavy, frothy, 10- to 50-µm Ca-Pb-P process product particles; one of these contains inclusions of U (fig. 3). The sample includes numerous 10- to 20-µm grains of monazite and zircon. The average monazite grain has 2- to 3-pct Th, and ranges up to 7 pct Th (fig. 4). High concentrations of Th (65 and 87 pct) are also associated with Si and Cl in two 3-µm grains. Grains of Mg-F contain scattered 1- to 3-µm inclusions of U (fig. 5). Other heavy grains in the sample are ilmenite, magnetite, and Fe process products. Light-weight particles include clays, calcite, and quartz.

BF1C 150- by 38-µm light fraction; polished section 3255. The light-weight particles include abundant quartz and feldspar. The Na-, K-, and Ca-feldspars average 20 to 150 µm. Other light-weight components include clay particles and 25-µm frothy siliceous process products composed of Fe, Mn, Ti, Ca, Al, and Si (fig. 6). Traces of heavy grains (pyroxene and/or amphiboles, Fe, process products composed of Fe, Ti, and Ca, and Fe-Mn process products) occur in this fraction.

BF1C minus 38-µm sample; polished section 3256. Heavy grains include 10- to 20-µm

monazite (with up to 12 pct Th), 5-µm rutile, and 5-µm zircon. Heavy Ba process products also contain Fe, Ca, K, S, and Si. The sample contains ilmenite and magnetite. The light-weight particles include quartz, feldspar, and clay. The sample also includes larger (100- to 500-µm) agglomerations of fines that may be the result of filtering wet samples during sizing procedures (fig. 7).

LV1C plus 150-µm heavy fraction; polished section 3257. Heavy material includes grains of pyroxenes and/or amphiboles, pyrite, Pb, Fe oxides, Ba process products, and Mg-F with U inclusions. The light-weight particles include siliceous process products and calcite (fig. 8).

LV1C plus 150-µm light fraction; polished section 3258. Light-weight particles include primarily calcite and quartz with some feldspar, siliceous process products, wood, and coal. Heavy particles include trace amounts of Ba process product

LV1C 150- by 38-µm heavy fraction; polished section 3259. Heavy particles include 50- to 100-µm Fe-Mn process products which contain varying amounts of Al, Si, P, Mn, and Fe. Other heavy grains are pyroxenes and/or amphiboles, ilmenite, Ba product, 10-µm monazite, 25-µm grains of zircon, Fe, and Fe oxides (fig. 9). Radioactive components include inclusions of U in Mg-F. The light-weight particles include quartz, calcite, and siliceous Fe-Mg-Mn-Si-Al-P process products.

LV1C 150- by 38-µm light fraction; polished section 3260. The light-weight particles include abundant quartz, some feldspar grains, and traces of clay and calcite. Heavy particles include 2-µm monazite grains locked with feldspar.

LV1C minus 38-µm sample; polished section 3261. The sample consists of agglomerated heavy zircon and abundant light-weight quartz and feldspar grains (fig. 10). The agglomerations may have resulted from filtering the product during sizing procedures.

SL2C plus 150-µm heavy fraction; polished section 3262. Heavy particles include abundant

100-µm Ba process products composed of Ba, S, Sr, Ti, and Si (fig. 11). The Ba product often includes intergrown Pb with traces of U (fig. 12). Other heavy constituents include Mg-F grains with inclusions of U (fig. 13), some pyroxenes and/or amphiboles, Fe, Fe-Mn-W-Al-Si-Pb process products, 15-µm Pb, and pieces of Pb-Sn solder. Medium- to light-weight particles include Fe oxides, and some round, 100- to 500-µm pieces of Fe-Ca-Al slags.

SL2C plus 150-µm light fraction; polished section 3263. The light-weight particles include primarily calcite with lesser amounts of wood, coal, and quartz. Traces of heavy grains include a Ba process product composed of W, P, Al, Ba, Pb, Sr, Ca, and S (fig. 14); Ra is suspected in this product. Other heavy grains include a glassy, frothy process product that contains Ba, Pb, Cr, Mg, Al, and Si, a few grains of zircon, Fe, and Fe oxides.

SL2C 150- by 38-µm heavy fraction; polished section 3264. Heavy particles include numerous grains of barite, Ba-Pb process products, 50- to 100-µm monazite (with approximately 8 pct Th) and Pb oxide (figs. 15-17). Numerous grains of U are locked in Mg-F (figs. 18-20); some of these U particles contain Pb, Fe, and possibly Ra. Other heavy grains include 30-µm zircon grains and particles of Al-Si-S-Ca-Fe-As-Ba-U process products. Another process product contains Mg, Al, S, P, Ca, V, Fe, Co, Ni, Cu, Pb, and possibly Th. Less-heavy constituents include pyroxenes and/or amphiboles, Fe oxide, and ilmenite (figs 18 and 19).

SL2C 150- by 38-µm light fraction; polished section 3265. The light-weight particles include Na- and K-feldspars, quartz, calcite, clay, and carbonaceous material. Heavy grains include a few Fe-Mn process products.

SL2C minus 38-µm sample; polished section 3266. Heavy particles include 1- to 10-µm grains of barite, zircon, rutile, bastnasite, and apatite. Light-weight particles include quartz and feldspar. Abundant large pieces of what may be filter cake (agglomerations of less than 1- to 5-µm grains of both heavy and light-weight constituents of the sample) from sample-sizing procedures remained intact through the mounting and polishing process (figs. 21-22).

BF3C plus 150-µm heavy fraction; polished section 3267. Heavy particles include small U and U-oxide inclusions in 100-µm Mg-F particles, 100- to 300-µm pieces of barite and 100-µm, frothy Ba process products that contain varying amounts of the elements Ca, Ti, Ba, S, Si, W, Fe, and Ni (fig. 23). Heavy constituents also include abundant Fe and Fe oxides, pieces of 100-µm Pb, and 30-µm Bi-Sn. Light-weight particles include 50- to 100-µm siliceous Cr-Fe-Al process products.

BF3C plus 150-µm light fraction; polished section 3268. Light-weight constituents include abundant coal, quartz, wood, shell fragments, calcite, and gypsum. Heavy particles include a few 500- to 1000-µm siliceous Fe-Mn process products and 100- to 200-µm grains of barite in calcite (fig. 24).

BF3C 150- by 38-µm heavy fraction; polished section 3269. Heavy particles include 100-µm barite grains and Ba process products that contains Pb, Mn, and S; zircon; 40-µm monazite (with 5 pct Th); and Fe and Fe oxides. Heavy constituents also include some grains of pyroxenes and/or amphiboles, ilmenite, sphene, and rutile or leucoxene. Light-weight particles include grains of K- and Na-feldspars and quartz (figs. 25-26).

BF3C 150- by 38-µm light fraction; polished section 3270. Light-weight particles include coal (some with apatite inclusions), wood, quartz, clay, and calcite. Heavy grains include trace 20-µm process products composed of siliceous Ba, Co, Mn, Ni, Cu, Fe, and Pb, and a few zircons.

BF3C minus 38-µm sample; polished section 3271. The sample consists of broken filter-cake agglomerates of fine material (less than 1 to 15 µm) which was undisturbed by the process of molding and polishing. These agglomerates are mixed with individual 25-µm quartz grains (fig. 27). Heavy grains include numerous 1- to 20-µm barite, Ba process products, ilmenite, and pyroxene and/or amphibole grains. Light-weight particles include quartz, calcite, and clay.

LV3C plus 150-µm heavy fraction; polished section 3272. Heavy particles include 100-µm barite and Ba and Fe-Mn process products (fig. 28), a 500-µm Cu-Zn particle, zircon,

pyroxenes and/or amphiboles, chromite, and serpentine. Light-weight constituents include traces of wood, quartz, calcite, feldspar, and coal.

LV3C plus 150-µm light fraction: polished section 3273. The sample contains particles of wood and quartz with small amounts of calcite, feldspar, and coal.

LV3C 150- by 38 µm heavy fraction: polished section 3274. Heavy grains include 50-µm ilmenite and magnetite, 30-µm zircon, liberated 10- to 20-µm monazite, barite, pyroxenes and/or amphiboles, Fe, and Fe oxides. Light-weight particles are primarily quartz (fig. 29).

LV3C 150- by 38-µm light fraction: polished section 3275. The sample is primarily composed of quartz, with small amounts of calcite, feldspar, and clay

LV3C minus 38-µm sample: polished section 3276. Heavy particles include Fe and Fe oxides, ilmenite, magnetite, barite, a grain of 1-µm Th-Si and a number of Ba process products. Light-weight particles include feldspar, quartz, and clay. Large (up to 1000 µm) agglomerations of 1- to 5-µm grains in the sample may be pieces of filter cake from sizing procedures.

SL3C plus 150-µm heavy fraction: polished section 3277. Heavy particles include numerous grains of barite and Ba process products, some with 10-µm inclusions of Pb-U (fig. 30). Also present in the heavy fraction are 500-µm grains of Pb oxide and grains of U locked in Mg-F particles (fig. 31). Medium-specific-gravity particles include Fe and some Mg-F with no detectable U

SL3C plus 150-µm light fraction: polished section 3278. Light-weight particles include calcite, quartz, wood, coal, clay, and siliceous process products. Trace heavy grains include process products composed of Mn, Fe, W, Pb, Si, Al, and possibly Ra.

SL3C 150- by 38-µm heavy fraction: polished section 3279. Heavy particles include numerous Mg-F particles with 1-µm inclusions of U, pyroxenes and/or amphiboles, ilmenite, Ba-Ca

process products, Pb, and sphene (figs. 32- 33). Heavy particles also include Ba process products composed of Ba, Pb, Ca, S, Sr, Cu, P, Al, and Si (figs. 34-35); this process product may have concentrations of U, Th, or Ra below 3 pct. The light-weight particles include quartz and calcite.

SL3C 150- by 38-µm light fraction; polished section 3280. Light-weight particles are primarily quartz, with a few K-feldspars and traces of clay. Trace heavy particles include process products composed of Mn, Fe, Ca, Ni, Ba, Pb, S, Ti, Al, and Si (fig. 36).

SL3C minus 38-µm sample; polished section 3281. Numerous small (less than 5 µm) heavy grains of Ba process product and fewer rutile and ilmenite grains are agglomerated with larger, light-weight quartz and feldspar in what may be pieces of filter cake that survived the molding and polishing process (figs. 37-38). Although detectable radioactive compounds were not identified by either EDX or WDX analysis, scintillometer counts for this sample were quite high and indicate that significant radioactive contamination is present

Implications for cleaning St. Louis North-County soils with minerals-processing technology

The results of this investigation show that the soils from the North County properties have some characteristics that are necessary for successful application of minerals-processing technology. However, the soils also exhibit characteristics that could make efforts to produce a significant volume of clean soil difficult.

Essentially all of the radioactive contamination is contained in process products that are distinct and liberated from the other soil constituents, and these products represent a small percentage of the sample. Most of the process products have a high specific gravity, and they represent a small fraction of the soil. About half of the radioactive contamination is in liberated mineral grains and porous process products.

On the other hand, the size distributions of these samples show that 54 to 80 pct of the soil is

minus 38 µm (RUST-CTC report); clays and clay-sized (less than 2-µm) particles comprise a significant percentage of the size fraction in some of the samples. The fine size distribution is not attractive for physical-separation methods; many of these methods become difficult or inefficient on feed that is less than 75 µm. About half of the radioactive contamination is locked within competent grains of process products.

Radioactive compounds were identified as heavy constituents in all three size fractions of most of the samples. Consequently, screening would not separate a significant volume of uncontaminated material.

The results of the heavy-liquid separation tests suggest that gravity separation could be a potential treatment option, although the fine size distribution would be a negative factor. Also, these separations were done only on the plus 150-µm and 150- by 38-µm fractions; separation of the minus 38-µm fraction, the bulk of the soil samples, was not attempted. Most of the process products and the associated radioactive contamination, as well as the ubiquitous Pb contamination, reported to the heavy fraction, and represents less than 7 pct of the sample weight. Most of the light fractions showed little radioactivity above background, and showed no detectable radioactive constituents in the SEM analyses, an indication that the light materials do not contain significant amounts of radioactive contaminants

Some of the light fractions contained traces of heavy process products, and some showed slightly elevated radiation as determined qualitatively by scintillometer measurements. These heavy, contaminated particles probably were entrained in the light fraction, a problem that would be magnified as the scale of operation increased. Some of the more siliceous process products may have specific gravities less than 2.90 (the specific gravity of the sodium polytungstate heavy liquid). The specific gravity of the bulk of the soil (quartz) is ~2.65. Separation of components by gravity diminishes rapidly as the difference in their specific gravities gets small.

The large surface area associated with the fine particles and the porous nature of some of the

contaminated particles would be beneficial to chemical extraction methods such as leaching. RUST-CTC reported encouraging results for preliminary chemical-extraction tests. The SEM photomicrographs show that much of the radioactive contamination would be exposed to an appropriate leachant. It remains problematical whether a chemical-extraction process can be optimized or conditions maintained that will allow the nearly complete removal of contamination necessary to produce a clean soil fraction that meets the clean-up criteria.

CONCLUSIONS

The results of mineralogical characterization studies on composite samples of soil from the North County properties of the St. Louis FUSRAP site show that radioactive contamination exists primarily in natural heavy minerals and heavy U-processing products. Uranium contamination is present primarily as locked metallic or oxide inclusions in Mg-F product. Thorium is present in high-Th monazite and Ba process products. Radium was not detected with the SEM and EDX/ WDX systems, but it is also likely present in the process products.

The particle size distribution of the soils indicates that physical separation of contamination by mineral-processing methods is probably not a viable volume-reduction option. Screening would be ineffective, and gravity separation would be difficult, although heavy-liquid separation results give some indication that it could work.

Chemical extraction offers the best option to successfully reduce the level of contamination in these soils to acceptable levels, but process parameters must be optimized to overcome potential problems such as leachant penetration and solids/liquid separation. The results suggest that additional bench-scale tests would be appropriate to investigate this option.

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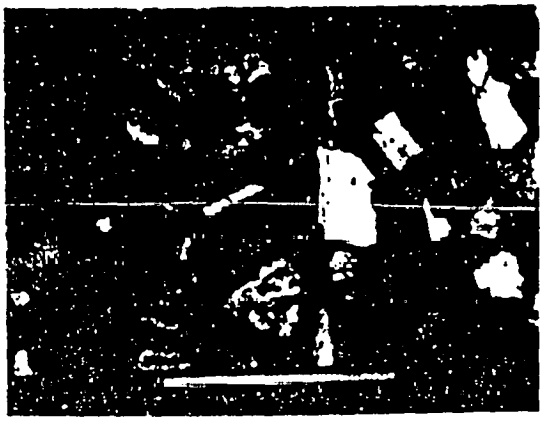

Figure 1. BF1C plus 150-µm heavy fraction. Bright Mn-Fe and Ba-Pb process products, medium Fe process products, and dark Mg-F process products with traces of bright U. Other dark particles include quartz, calcite, and siliceous process products. Scale bar is 1000 µm.

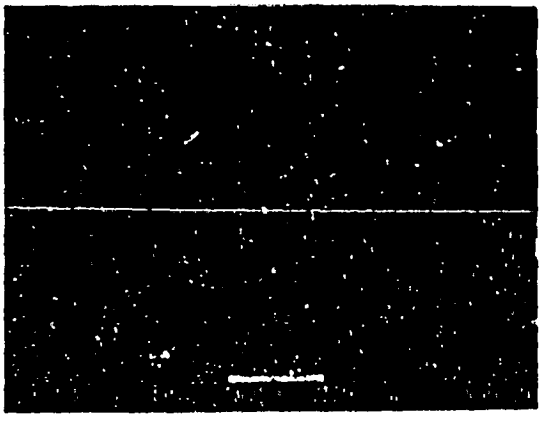

Figure 2. BF1C plus 150-µm light fraction. Typical light-weight mineral assemblage of quartz, calcite, carbonaceous material, and siliceous process products. Scale bar is 1000 µm.

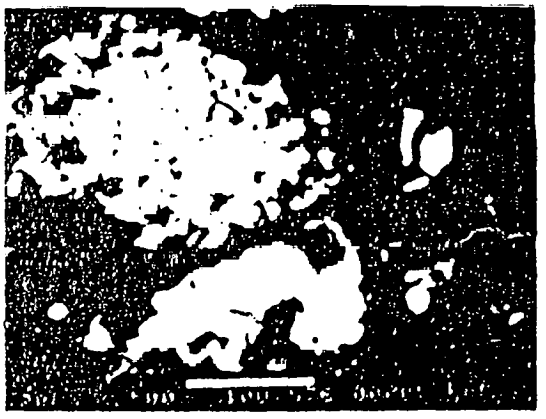

Figure 3. BF1C 150- by 38-µm heavy fraction. Bright Ca-Pb process product at top contains U inclusions. Fe-Fe oxide particle is below. Scale bar is 10 µm.

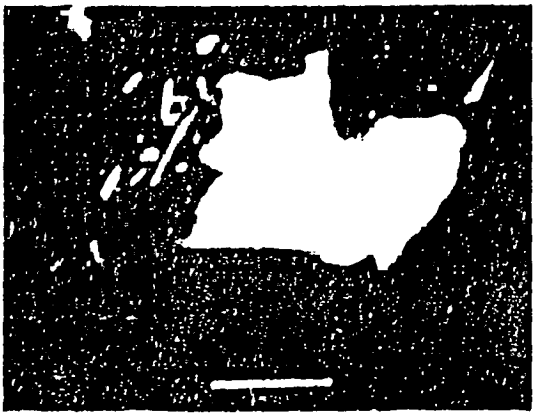

Figure 4. BF1C 150- by 38-µm heavy fraction. Bright high-Th monazite locked with darker rutilated quartz. Scale bar is 10 µm.

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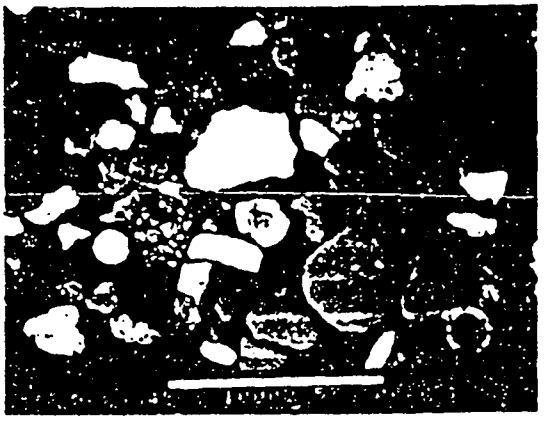

Figure 5. BF1C 150- by 38-µm heavy fraction Typical particle assemblage Bright Ca-Pb process products magnetite, zircon, and monazite grains medium Mg-F process products with small bright spots of U, and dark quartz and mottled particles of quartz and calcite Scale bar is 1000 µm

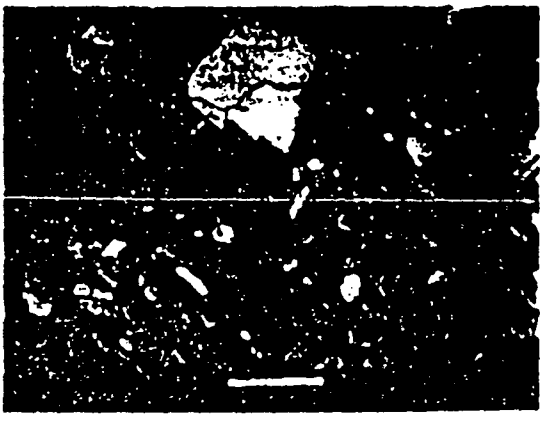

Figure 6 BF1C 150- by 38-µm light fraction Lightweight assemblage of dark feldspars and quartz with traces of bright pyroxenes and/or amphiboles Scale bar is 100 µm

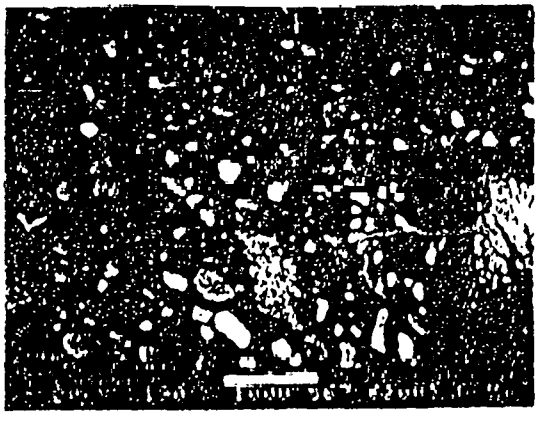

Figure 7 BF1C minus 38-µm sample Assemblage of dark feldspars, quartz, and clay, and bright monazite and zircon grains Large (greater than 50 µm) particles are agglomerations of smaller particles Scale bar is 100 µm.

Figure 8 LV1C plus 150-µm heavy fraction. Bright central Pb particle surrounded by bright Ba-Ca process products and monazite grains. Medium Mg-F process products contain traces of U. Darkest particles are siliceous process products. Scale bar is 1000 µm.

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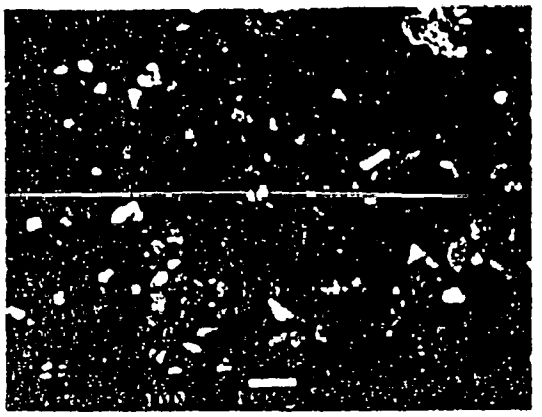

Figure 9 LV1C 150- by 38-µm heavy fraction Bright elongate and large mottled Fe-Mn product and small bright rounded zircon, monazite, barite, and ilmenite grains Medium grains are pyroxenes and/or amphiboles, and dark grains are Mg-F and siliceous process products Scale bar is 100 µm

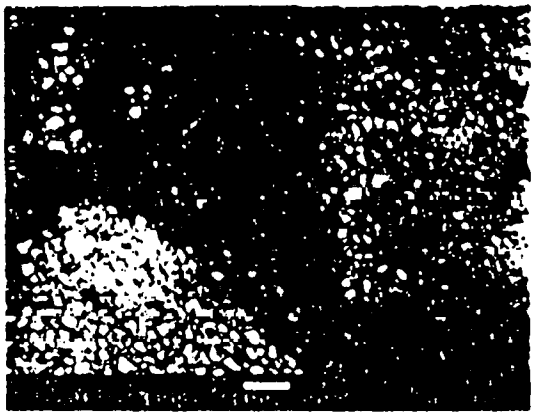

Figure 10 LV1C minus 38-µm sample Agglomerated mixture of medium quartz and feldspar grains and bright zircon grains Scale bar is 100 µm

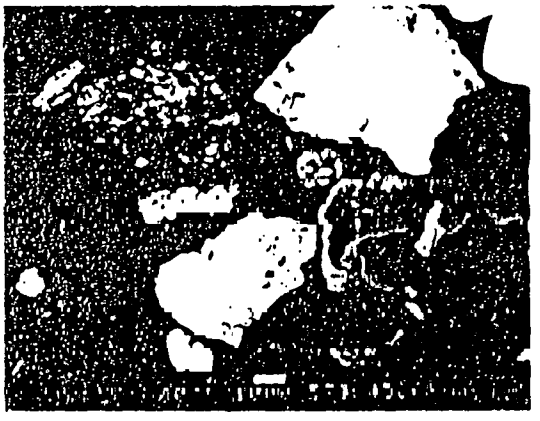

Figure 11 SL2C plus 150-µm heavy fraction A medium Ba process product mottled with bright Pb and bright barite grains in an assemblage of darker Mn-Fe process products and Fe process products, one with bright Pb stringers Scale bar is 100 µm

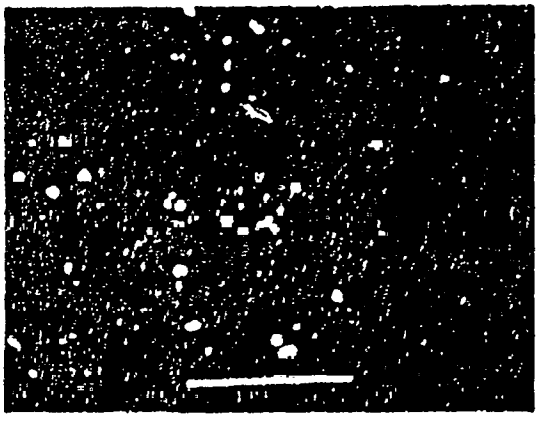

Figure 12 SL2C plus 150-µm heavy fraction. Bright Pb-U grains in a Ba process product. Scale bar is 100 µm

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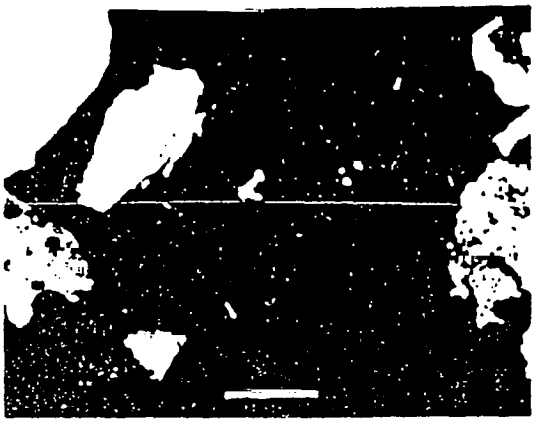

Figure 13 SL2C plus 150-µm heavy fraction Typical dark Mg-F process product with bright inclusions of U Bright surrounding grains are Fe and Fe oxides Scale bar is 100 µm

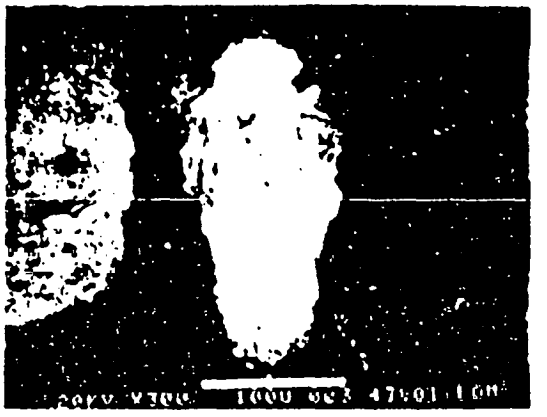

Figure 14 SL2C plus 150-µm light fraction. Rare bright, heavy Ba process product with darker quartz and calcite grains in low-specific-gravity fraction Scale bar is 100 µm

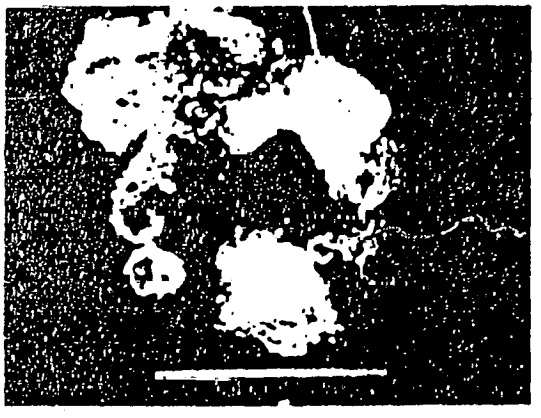

Figure 15 SL2C 150- by 38-µm heavy fraction Ba-Pb process product Brighter portions are higher in Pb Scale bar is 100 µm.

Figure 16 SL2C 150- by 38-µm heavy fraction. Large bright monazite and smaller bright barite grains in an assemblage of darker Fe, Fe oxides, Fe process products, and pyroxenes and/or amphiboles. Scale bar is 100 µm.

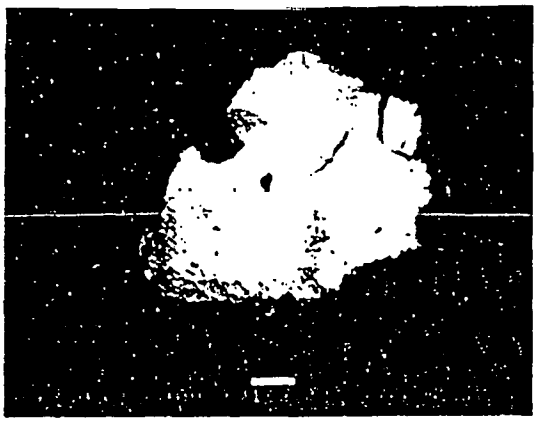

Figure 17 SL2C 150- by 38-µm heavy fraction Grain of Pb oxide Scale bar is 10 µm

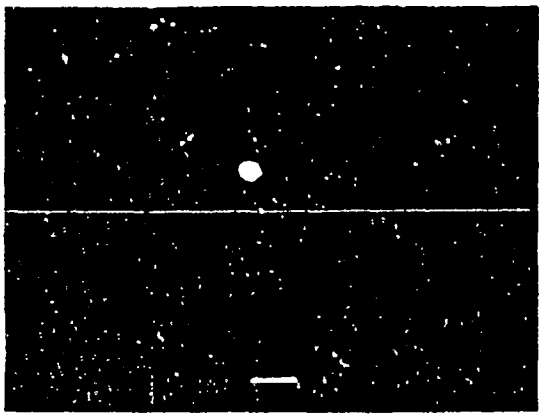

Figure 18 SL2C 150- by 38-µm heavy fraction Bright U inclusion in a Mg-F process product Scale bar is 10 µm

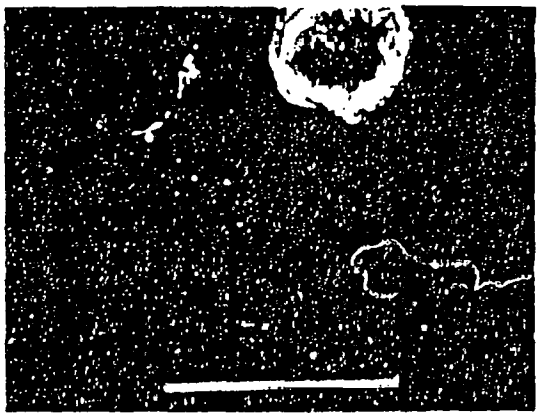

Figure 19 SL2C 150- by 38-µm heavy fraction Dark Mg-F process product with inclusions of bright U, medium pyroxenes and/or amphiboles, and bright Ba process product Scale bar is 100 µm

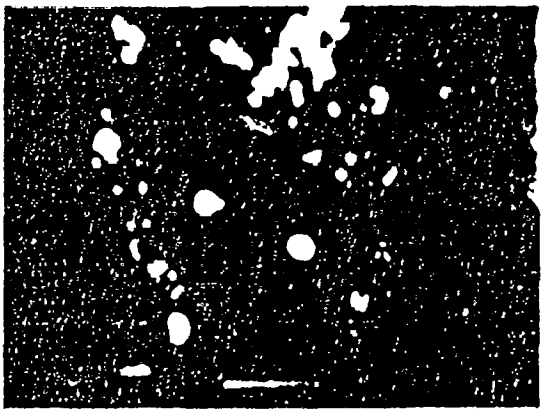

Figure 20 SL2C 150- by 38-µm heavy fraction. Magnified U inclusions in a Mg-F process product. Scale bar is 10 µm

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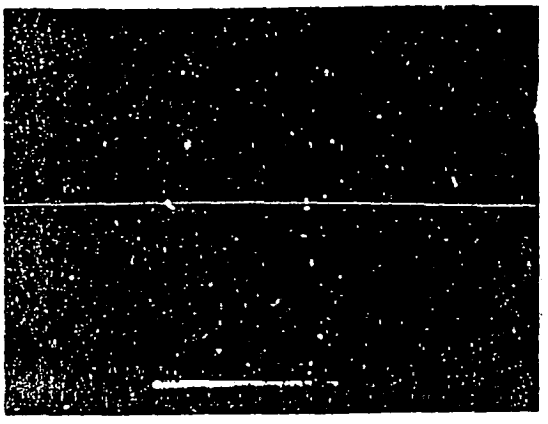

Figure 21 SL2C minus 38-µm sample Agglomeration of less than 1- to 5-µm particles of bright zircon, barite, and rutile and dark quartz and miscellaneous silicates with individual grains of 10 to 30-µm quartz Scale bar is 1000 µm

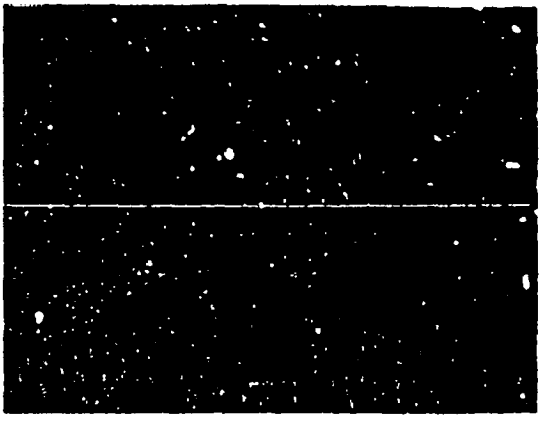

Figure 22 SL2C minus 38-µm sample Magnified view of agglomerations of fine particles in figure 21 Scale bar is 100 µm

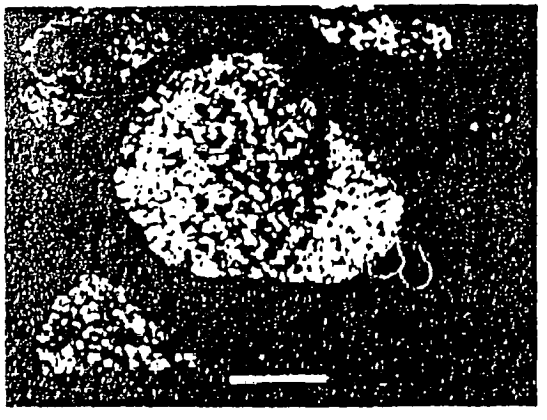

Figure 23 BF3C plus 150-µm heavy fraction Bright Ba-Ca process products and medium Mg-F process product with bright U Scale bar is 100 µm

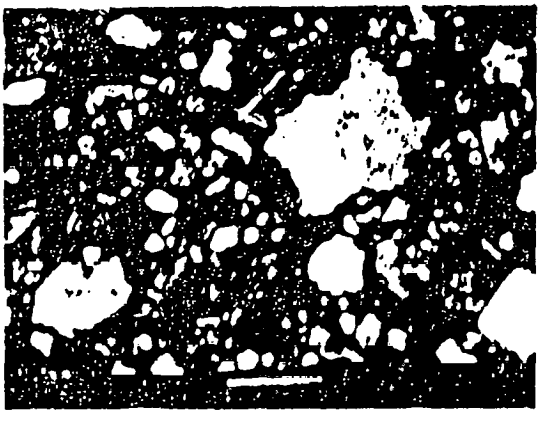

Figure 24 BF3C plus 150-µm light fraction. Bright frothy Mn-Fe process products and rounded Ba-Ca products with abundant dark carbonaceous material, quartz, and calcite. Scale bar is 1000 µm.

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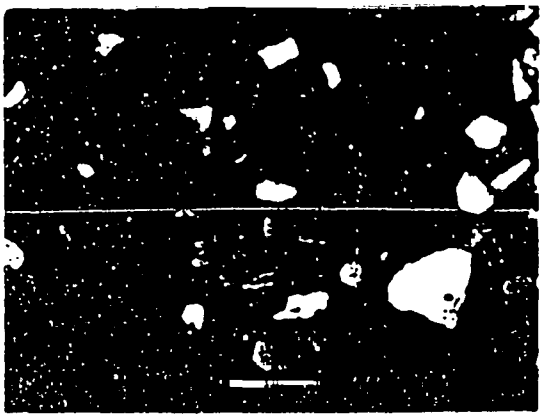

Figure 25 BF3C 150- by 38-µm heavy fraction. Assemblage of bright central monazite grain, smaller bright zircon and barite grains, larger bright magnetite, Fe-oxide, and ilmenite grains, medium pyroxenes and/or amphiboles, and dark quartz and feldspar. Scale bar is 100 µm.

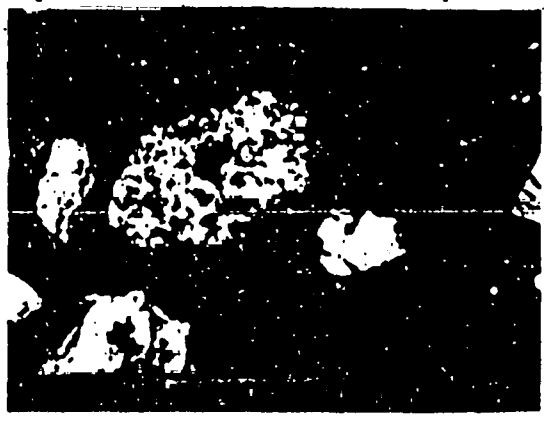

Figure 26 BF3C 150- by 38-µm heavy fraction. Large Ba-Ca process product surrounded by bright ilmenite and magnetite grains, medium pyroxenes and/or amphiboles, and dark quartz. Scale bar is 100 µm.

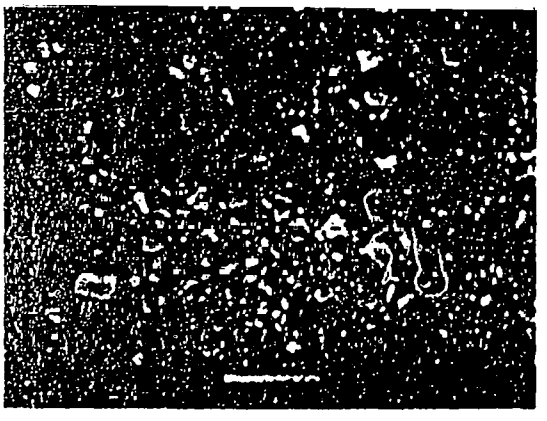

Figure 27 BF3C minus 38-µm sample. Agglomerated medium quartz grains and bright barite grains. Scale bar is 100 µm.

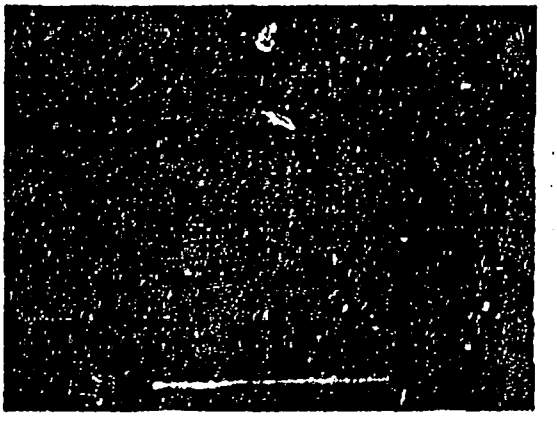

Figure 28 LV3C plus 150-µm heavy fraction. Bright barite grain at top with Mg-F product and Mg-Si minerals. Scale bar is 1000 µm.

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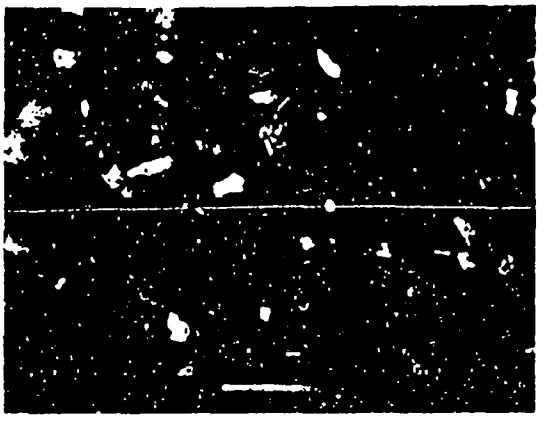

Figure 29. LV3C 150- by 38-µm heavy fraction. Large, bright ilmenite and magnetite grains with smaller bright zircon and monazite grains in collection of medium pyroxenes and/or amphiboles Scale bar is 100 µm

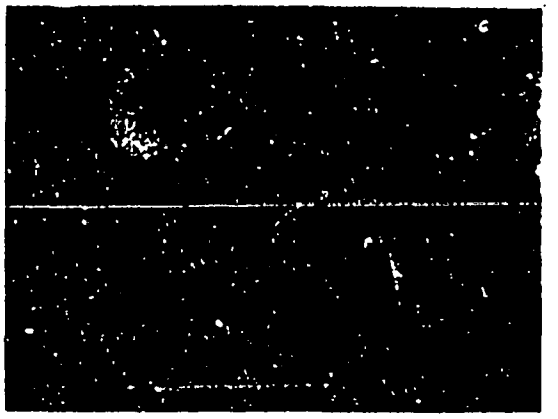

Figure 30. SL3C plus 150-µm heavy fraction. Bright Pb-U inclusions in Ba-Ca process product in lower center Surrounding grains are also process products Scale bar is 1000 µm.

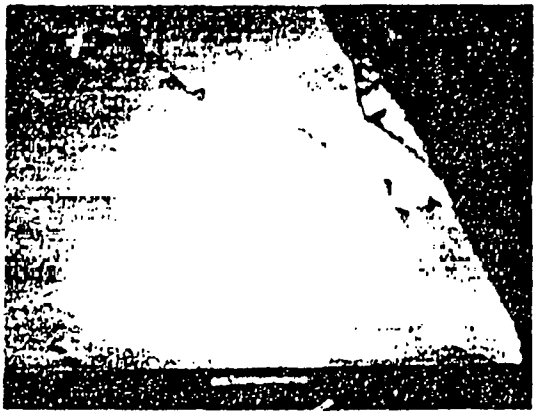

Figure 31. SL3C plus 150-µm heavy fraction Bright U grain in Mg-F process product Scale bar is 10 µm

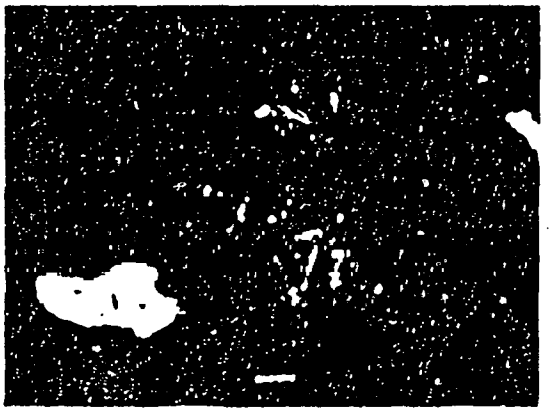

Figure 32. SL3C 150- by 38-µm heavy fraction. Bright U inclusions in dark Mg-F process product. Bright mottled grains of Ba-Ca process product, medium ilmenite grain, and dark Mg-F process product. Scale bar is 10 µm.

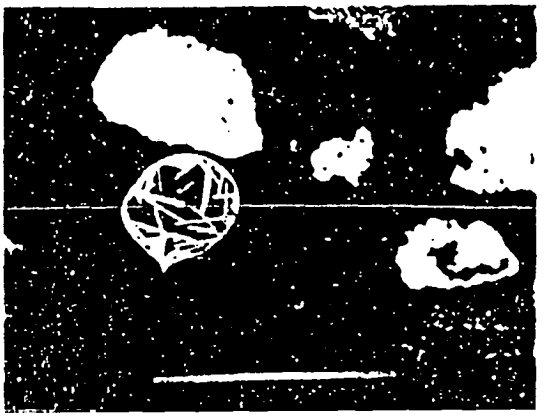

Figure 33. SL3C 150- by 38-µm heavy fraction Assemblage with bright needle-like Pb; bright, frothy Ba-Ca process products; and dark Mg-Fe process products and pyroxenes and/or amphiboles Scale bar is 100 µm

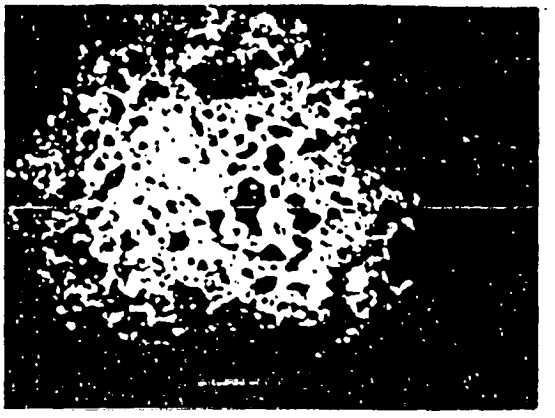

Figure 34 SL3C 150- by 38-µm heavy fraction. Bright Ba-Pb-Ca process product. Scale bar is 10 µm

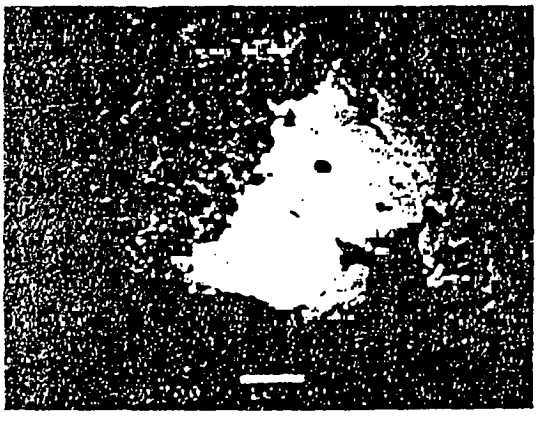

Figure 35. SL3C 150- by 38-µm heavy fraction. Composite particle with solid bright Pb-Ca-Sr-Th(?) process product locked with common Ba-Ca process product. Scale bar is 10 µm.

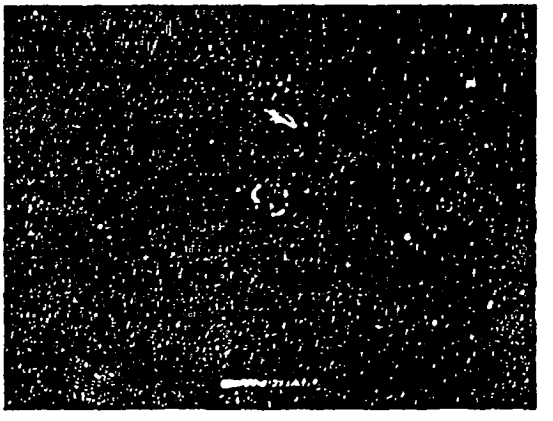

Figure 36. SL3C 150- by 38-µm light fraction. Bright heavy Mn-Fe process product at center with darker quartz and feldspar. Scale bar is 100 µm.

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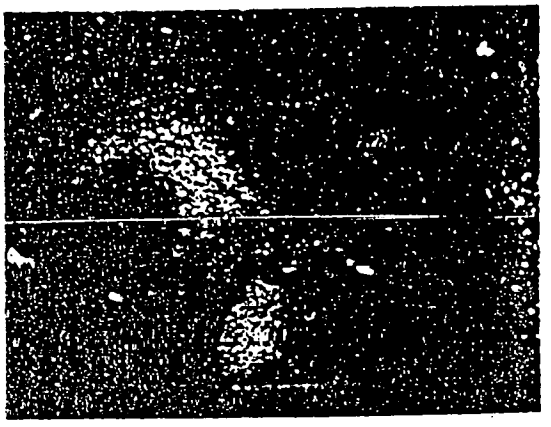

Figure 37. SL3C minus 38-µm sample. Agglomerated bright fine-grained (1- to 5-µm) Ba process product and darker quartz. Separate medium quartz grains and bright ilmenite grains are larger (5 to 20 µm). Scale bar is 100 µm.

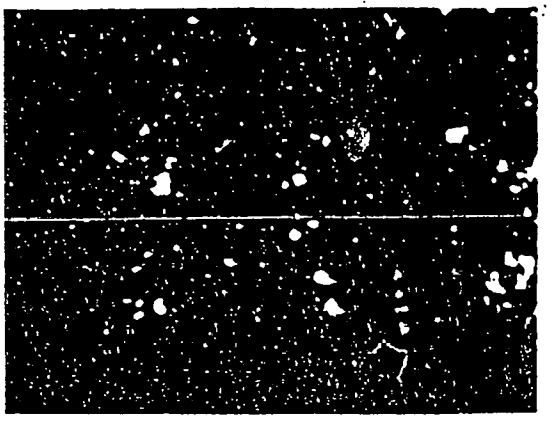

Figure 38. SL3C minus 38-µm sample. Magnified view of the mixed sample in figure 37 has 1- to 5-µm grains of bright Ba product and darker quartz. Scale bar is 10 µm.

Formerly Utilized Sites Remedial Action Program (FUSRAP)

ADMINISTRATIVE RECORD

for the St. Louis Site, Missouri

U.S. Department of Energy