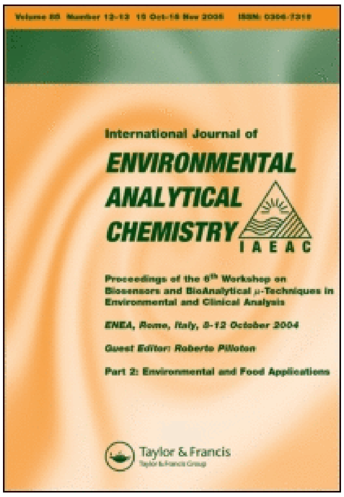

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MULTI-ELEMENTAL ANALYSIS IN SIZE FRACTIONS OF FINE-GRAINED SOLID RESIDUE OF ORE GRINDING

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Suspensions of fine-grained material originated from a former uranium mine in Central Germany and deposited in a settling plant were investigated. Total concentrations in the waste material ranged from 150 mg kg^{-1} (Ni), 215 mg kg^{-1} (As), 285 mg kg^{-1} (U), 290 mg kg^{-1} (Pb) to 1230 mg kg^{-1} (Zn). In order to find a correlation between particle size and the concentration of selected elements (As, U, Cu, Zn, Ni, Mn, Fe and Pb) the material was separated into different particle size fractions by independent procedures: (I) subsequent step-by-step fractionation (*standard cascade*) and (II) on-line multistage membrane filtration (OMFD). Using ICP-AES and ICP-MS the concentration of these elements in the particles, in solution and in the material deposited on filter (after dissolution with *aqua regia)* were determined. The main advantage of OMFD over cascade filtration exists therein, that the clogging of the membranes by particles is diminished indicated by a significant increase of the yield of particles in the individual fractions. It was shown that the sample preparation is very important for size fractionation of fine-grained materials. Surfactants, like sodium metaphosphate, led to an increase of the concentration of several elements in the dissolved form. This could be mainly attributed to the dissolution of analytes which were bounded on the particle surfaces as shown for uranium.

It was found that As and Pb are homogeneously distributed in all size fractions of the uranium processing waste. The concentration of the elements Fe, Zn, Cu and Mn varied with particle size. They showed a similar pattern in size distribution. The highest amounts of these elements were found in the particular fraction > 8 μm. High amounts of U are sorbed on the particle surface.

Keywords: Tangential ultrafiltration; particle size; heavy metals; uranium ore tailings; ICP-AES; ICP-MS

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INTRODUCTION

Pollution of the environment by metals and metalloids is a world-wide problem. A major source for contamination is the ore – mining and processing. As shown below, the uranium ore processing at selected sites in Saxon (Germany) yielded ultra-fine grained residues predominantly deposited in settling plants. The total concentration of metals and metalloids in fine-grained residues is of general relevance to assess the potential toxicity. Of importance is also to determine the partition of heavy metals fixed or in the mobile fractions to explain in which amount and form the translocation occurs. Association of metal ions with particular matter may accelerate or inhibit the rate of transportation of contaminants.

Fine-grained materials can be present and be transported depending on their physical and chemical properties (size, geometry, density, surface activity, functionalities, stability) in aquatic systems. They can be involved in exchange and sorption processes with soluble components and ions. For the characterization and classification of deposited waste products not only the particle size distribution but also the number of particles, their masses, compositions, etc. as a function of the particle size have to be investigated. The determination of major components as well as trace elements in size-classified aqueous fractions is one step to the risk assessment[1–4]. Until today only insufficient knowledge gives over the toxic or ecotoxicological effects of particularly bound heavy metals or metalloids. One thesis is that the free metal activity in water controls the rate of metal uptake as well as any associated biological effects[5]. That means the toxicological effect of particularly bonded metalloids and metals is also depending on partitioning between dissolved and particulate phases[6] an thus on the binding of these species to the surface of the particles.

The fractionation of particular matter, its separation from dissolved compounds and preconcentration requires the application of methods based on physical separation. Only a few of techniques, like membrane filtration, sedimentation, centrifugation, field-flow fractionation, and size exclusion chromatography, are suitable to separate larger from smaller particles in aqueous solution with a minimum perturbation of natural equilibrium[7–9].

To receive an information over the size distribution of selected analytes, two different techniques for the preparation of suspensions as well as two different methods for membrane filtration were employed and compared in this work.

EXPERIMENTAL

Material

The residues studied in this work originate from a former processing of uranium ores in Central Germany. The original ore was predominately an uraniferous black shale. The ores were ground and treated by the soda-alkaline leaching process to extract the uranium. During processing $BaCl_2$ was added to remove radium by co-precipitation with $BaSO_4$. Approximately 850,000 m^3 of the waste of this process was deposited in an abandoned uranium tailings pond known as Daenkritz 2 (near Zwickau, Saxon) over a period of 10 years (1950–1959).

Characterization of solid original material

X-ray diffraction studies of this silty material indicated the predominance of silicates, mainly in form of illite with small amounts of quartz[10].

The total contents of selected elements were determined in dried material (105°C) by wavelength disperse x-ray fluorescence on a SRS 3000 (SIEMENS AG) using pellets of the solid samples mixed with 20 % w/w stearine wax (Hoechst) as binder and subsequently pressed at 200 MPa. To improve the accuracy of the determination of the major components pellets based on fusion with $Li_2B_4O_7$ (Merck)(mass 1 + 7) were prepared.

Additionally, the *aqua regia* soluble content of metals was determined according to German DIN procedure 38 414-S7[11] (compare Method A in: European Standard, Draft prEN 308300 [12]) using ICP-AES with pneumatic nebulization (Spectroflame, Spectro A.I.).

The first fractionation of the original material was performed by dry sieving in the three size ranges: > 100 µm, 100 –32 µm, < 32 µm. Based on the sieved fraction <32 µm the subsequent separation procedures for particle size ranges from 0.025 to 8 µm were carried out.

Apparatus and procedures

The device used for size fractionation of water components by stepwise tangential flow membrane filtration described in[13–16] was utilized in this work. The results were compared with those obtained by a step-by-step filtration (*standard cascade*) using a Pyrex-filter holder (47 mm). In both cases polysulphone membranes (Millipore) with pore sizes of 8, 1.2, 0.45, 0.22 and 0.025 µm, respectively, were used.

The resulting fractions (both the suspensions and the filters with deposited material) were analyzed. To stabilize the aqueous solutions after fractionation (the volume of each fraction ranged between 10 and 30 mL) 1 mL of nitric acid suprapur (65%) (Merck) was added. The acidified solutions were diluted to a final volume of 50 mL with deionized water. The concentration of the elements in solution were determined to be in the µg L^{-1} range. For the determination of Fe, Zn, Cu, and Mn ICP-AES detection was sensitive enough. The concentration of U was in the range of the limit of quantification (0.12 mg L^{-1}) – limit of detection LOD 0.03 mg L^{-1} – of the ICP-AES using the emission line 424.167 nm. All other lines could not be used due to their interference by matrix components. To improve the accuracy of the uranium determination the results obtained by ICP-AES were compared with those obtained by ICP-MS. To perform the simultaneous determination of As, Pb and Ni the ICP-MS technique (ELAN 5000, Perkin-Elmer) with cross-flow nebulization was chosen.

The filters with the deposited material were transferred into quartz tubes used for dissolution by *aqua regia* (Behrotest, Behr). After dissolution the supernatant was separated by centrifugation (10 min, 5000min^{-1}). The solutions were diluted to a final volume of 50 mL with deionized water.

Two different procedures to prepare suspensions of the material were employed.

Procedure A

250 mg of the sample (fraction <32 µm) were suspended in 10 mL of deionized water (Milli Q, Millipore) by shaking in a bottle shaker for 24 h.

Procedure B

250 mg of the sample were treated in 10 mL of an aqueous solution containing 0.33 % *Graham's salt* (sodium metaphosphate, Merck) as surfactant in an ultrasonic bath (Transonic TS 420, Elma) for 2 minutes.

In addition the influence of the duration of the ultrasonic pretreatment on the solubility of different elements in sodium metaphosphate solution was tested. To study this influence an ultrasonic homogenizer, SONOPULS GM 200 with a titanium sonotrode MS 73 (BANDELIN electronic, Berlin) with a fixed energy (50 W, 20 kHz) was used.

RESULTS AND DISCUSSION

As shown in Table I the main components are Si, Fe, Al, Ca, and Mg. The concentrations of elements classified as environmentally relevant Cu, Ni, Pb, U, and As were in a range between 150 and 300 mg kg^{-1} and for Zn 1250 mg kg^{-1}, that means at levels which are of interest to estimate the risk of mobilization and translocation of this material.

TABLE I Composition of deposited material of the uranium ore preparation from Daenkritz 2

analyte	*concentration [mg kg^{-1}]*				
	total		*sieved fractions*		
			< 32 µm	*32 – 100 µm*	*>100 µm*
	WDXRF	ICP AES[a]	ICP-AES[a]	ICP-AES[a]	ICP-AES[a]
Al	32100	32000	34600	32000	34000
As	215	225	180	171	215
Ca	19700	18800	20650	18360	15000
Cr	130	65	59	56	70
Cu	165	165	826	549	125
Fe	43200	37300	35000	32700	33100
Mg	18000	16900	14870	14100	14000
Mn	780	750	720	710	535
Ni	150	140	110	110	120
P	1150	1130	1150	970	1020
Pb	290	275	220	230	160
Si	258000				
Th[b]	13	14	41	29	23
U[ab]	285	210	230	230	220
Zn	1230	1250	1340	1170	1000

a. ICP-AES.
b. ICP-MS: concentration in leachates using *aqua regia*.

The comparison (Table I) of the analytical data obtained for the concentration of As, Cu, Mn, Ni, Pb, and Zn in the original sample using WDXRFA and ICP-AES shows reasonably good agreement. Chromium and uranium both present as oxoanions were determined with somewhat lower recoveries after *aqua regia* digestion. This means that the elements except those mentioned above seem to be quantitatively leachable from the tailings material by *aqua regia*.

To find out whether the chemical composition varies with the grain size of the solid particles fractions of > 100 µm, 100 –32 µm, < 32 µm separated by dry sieving were analyzed. The values in Table I indicate that the elements (with exception of Cu) are homogeneous distributed in the three sieved fractions of the tailings material. It can be suggested that the fraction < 32 µm grain size (approx. 15% of the total mass) represents the same composition like the bulk of the tailings material. Based on this sieved fraction (<32 µm) the proposed procedures A and B for particle fractionation in the size range 0.025 to 8 µm were used for further investigations.

Sample pre-treatment

To operate under identical conditions the influence of the sample pretreatment on the recovery was estimated by analyzing the concentration of selected elements in the filtrate using the one step filtration procedure with < 0.22 µm pore size. As shown in Figure 1 the application of sodium-polyphosphate and ultrasonic treatment (*procedure B*) led to a substantial increase in the solubility of the trace elements in contrast to the solubility of the main components (approx. 2 % w/w for Fe). Compared with the total concentration of the analytes in the solid material concentrations ranged between approx. 15 % w/w for Ni, As and 32 % w/w for U in the fraction < 0.22 µm as dissolved and suspended matter. The analytical results for the aqueous fraction using *procedure A* shows that the elements U, Mn, As, and Ni are slightly soluble in water in comparison to the totally fixed components Fe, Cu, Zn, and Pb.

The considerable increase in solubility seems to be affected by polyphosphate as surfactant by complexing and/or ion exchange supported by ultrasonic treatment.

Addition of sodium metaphosphate increases the repulsive forces between the particles[10,17]. The advantage of employment of this surfactant is that the particles are not destroyed. The increase in the concentration of analytes in solution results essential from the desorption of analytes sorbed on the surface of the particles in the original material.

Additional investigations were done to study the influence of ultrasonic treatment on the desorption process. As shown in Figure 2, without any additional US treatment (shaking for 10 minutes) already considerable quantities of As, Pb, Ni, U, Mn, Cu, Zn and Fe are dissolved by adding sodium metaphosphate as surfactant. However, a significant increase of the solubility with increasing duration of US treatment. was observed only for Ni, As, Cu, and U.

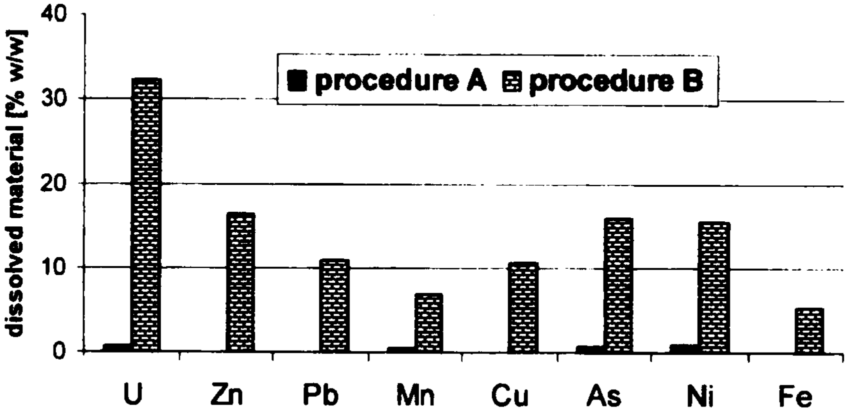

FIGURE 1 Influence of sample preparation on the dissolution of analytes (fraction < 0.22 μm) using one-step filtration

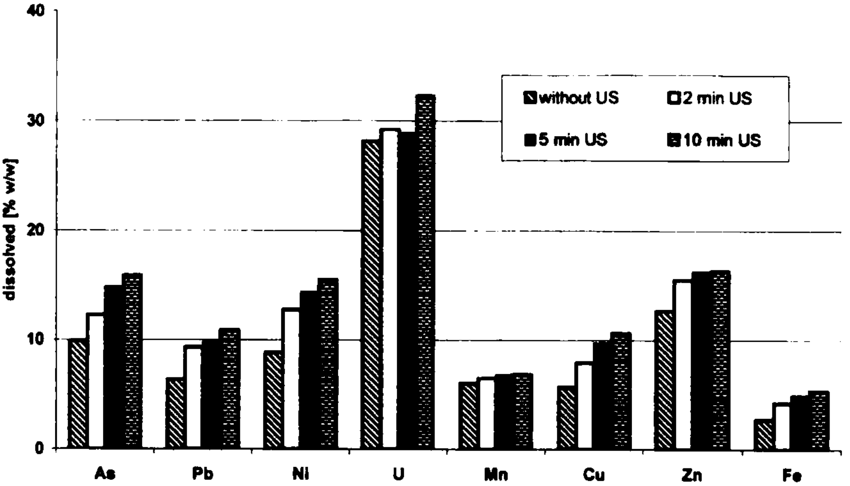

FIGURE 2 Influence of ultrasonic treatment procedure on the solubility of selected elements given as dissolved portion (%w/w) related to the total concentration (xrf – data)

To calculate the balance between dissolved and particle bonded material the concentration of uranium was determined in the solid material before (original sample) and after sodium metaphosphate treatment (in the filter cake) by X-ray fluorescence analysis. The concentration in the known amount of filtrate was determined by ICP-AES. As shown in Figure 3 approximately 70 % w/w of uranium is bonded in the particles.

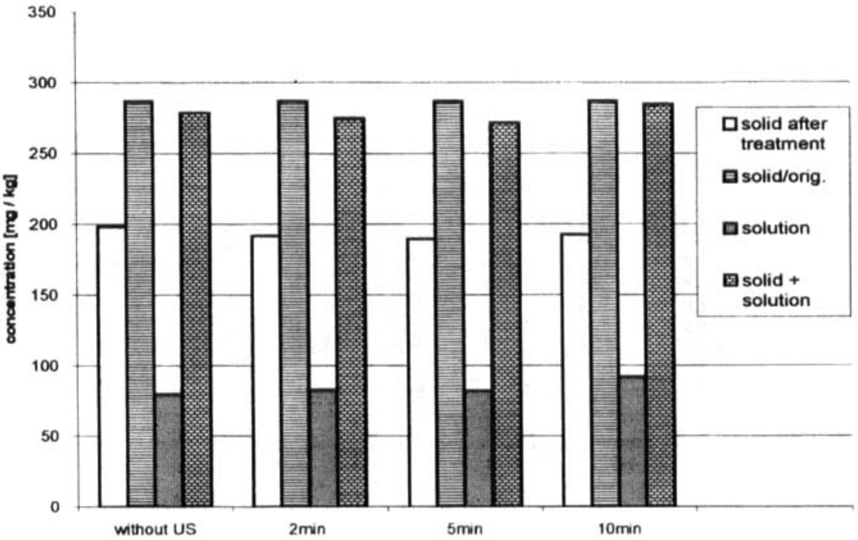

FIGURE 3 Comparison of the concentration of uranium in the solid material before and after sodium metaphosphate treatment ultrasonically assisted

Comparison of filtration techniques

A cascade of conventional filtration cells mostly applied in the fractionation of particulate matter suffers from several disadvantages e.g. the formation of coagulate layers, the sedimentation of particles on the filter surface and clogging phenomena. Therefore, an on-line multi-stage membrane filtration device (OMFD) described in[13–16] with a slightly modified geometry of the separations chambers was tested to minimize these phenomena. Previous investigations were performed with planar and equidistant chambers which led to phenomena mentioned above. The modification of the chamber consists of the application of a slightly conical upper part of the chamber to guarantee a more homogeneous radial flow profile in the channels of the chamber.

The following investigations were carried out with suspended fine-grained material prepared by *procedure B*.

Particularly for particles with larger diameters, it can be shown clearly (Figure 4) that with the application of OMFD substantially smaller quantities of particles are deposed on the filters.

This means that the results obtained with the conventional cascade technique are strongly influenced by both agglomeration of smaller particles during the filtration process and clogging of the membranes. These processes are accompa-

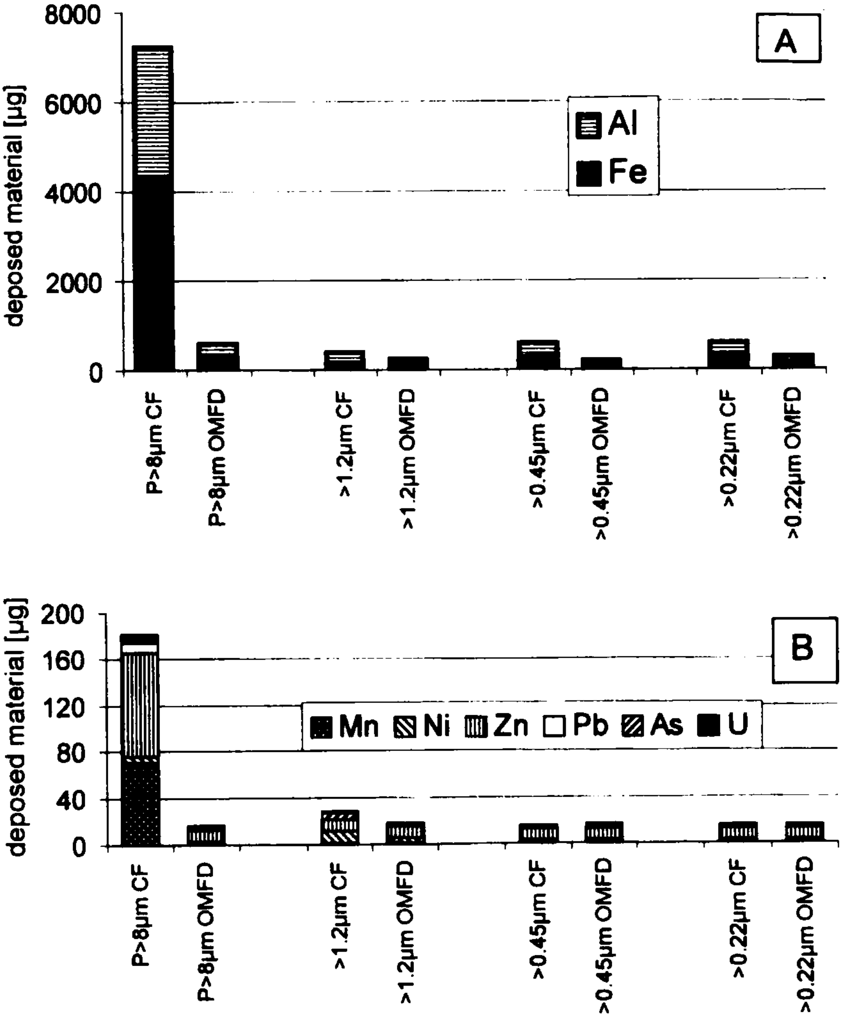

FIGURE 4 Comparison of cascade filtration (CF) and OMFD filtration used for fractionation: amount of deposed material on membranes after fractionation (A) main components; (B) trace elements

nied by an advanced adsorption of dissolved components at the filter cake. Figure 5 shows that the separation of the dissolved components (total amount of the analytes in the fraction <0.22 µm) from the solid material is substantially improved with application of OMFD in comparison to the cascade technique.

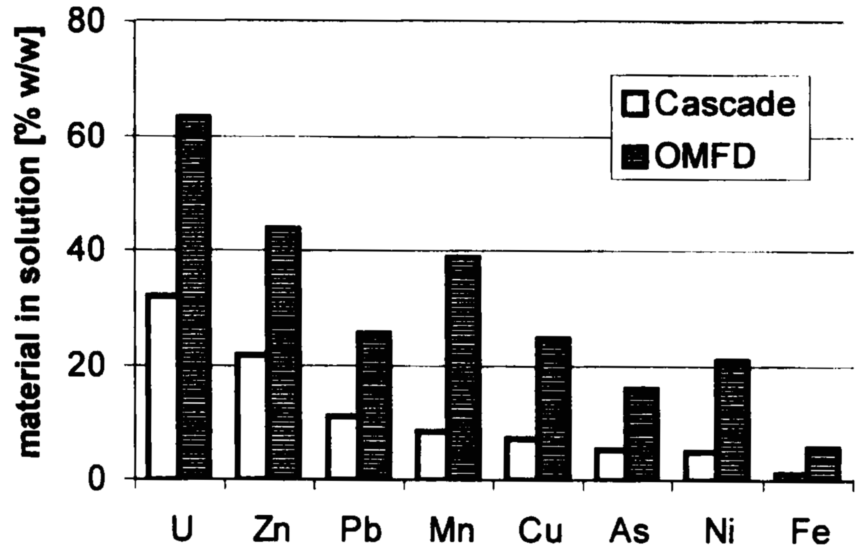

FIGURE 5 Comparison of cascade filtration (CF) and OMFD filtration used for fractionation: Percentage of total element amounts detected in solution (dissolved and suspended as particles in the fraction < 0.22 μm)

Application of OMFD

The Daenkritz material was suspended as described in *procedure B* and subsequently OMFD-fractionated. The separated particles of each size fraction and the solution (< 0.025 μm) were analyzed.

The total amounts of selected analytes in each fraction are given in Figure 6. As and Pb are homogeneously distributed within all the fractions.

Iron, zinc, copper, and manganese show a similar pattern. The suspended material in the particle fraction > 8 μm contains a high portion of these elements. There is also a relatively high amount of these elements in the fraction < 0.025 μm. High portions of uranium (17%) and copper (15 % related to the solid material) were also determined in the dissolved fraction < 0.025 μm indicating the high mobilization rate of these elements in sodium metaphosphate solution. Compared with the results presented in Figure 2, the differences in the concentrations can be attributed to the capabilities of the different methods used.

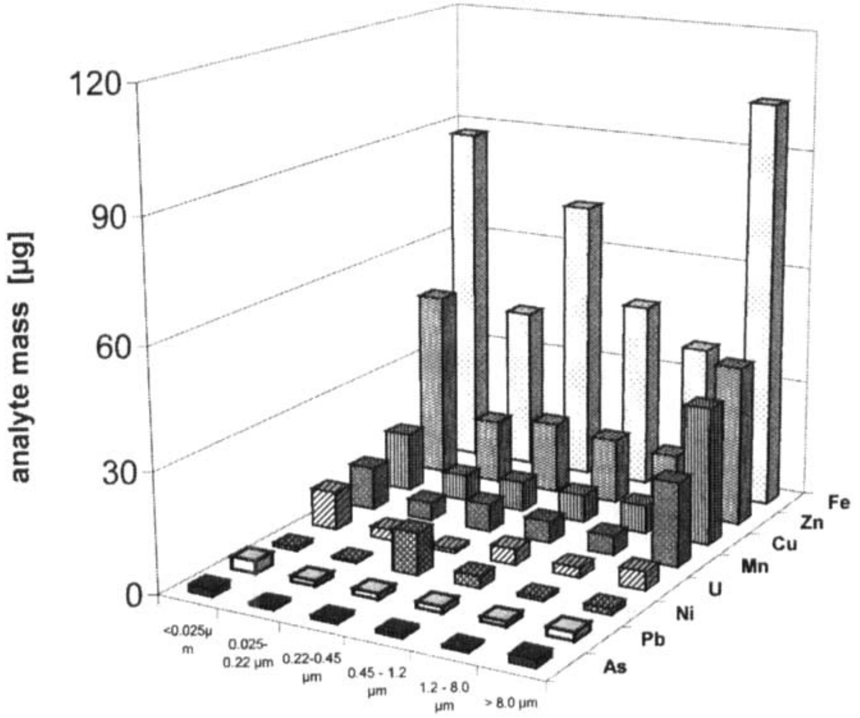

FIGURE 6 OMFD separation of Daenkritz material: Pattern of the amounts of selected elements in particle fractions; values corrected by the mass containing in solution

CONCLUSION

A specially designed on-line fractionation device OMFD was employed for multistage size fractionation of suspended fine-grained waste of uranium processing. Based on optimized flow conditions it was possible to separate such fine-grained materials into the particular and soluble components (five size fractions between > 8 µm and > 0.025 µm and the dissolved phase).

The main advantage of the OMFD over cascade filtration exists therein, that the clogging of membranes by particles is reduced. That results also in a significant increase of the yield of particles in the individual fractions. Using the OMFD technique a size fractionation pattern of selected heavy metals in a fine-grained material was realized.

It was also shown that the sample preparation is very important for size fractionation of fine-grained materials. Especially the addition of surfactants, which are also suitable complexing agents, like sodium metaphosphate, led to an increase of the concentration of several elements in the dissolved form. This could be mainly attributed to the dissolution of analytes which were bounded on the particle surfaces as shown for uranium.

In following investigations is planned to compare the results obtained here with those using field flow fractionation to get additional information about the particles. All these data will be used to estimate ecotoxicological effects of particle-bonded heavy metals.

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