Scanning Electron Microscopy Analysis of CRUD-material in the PSI-Hotlab

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Abstract

The nuclear reactor water chemistry has evolved during the last decades with the introduction of new processes as Zn injection for example. In consequence, interest in the detailed analysis of the CRUD material has increased. If the chemical analysis of the CRUD with ICP-MS stays the main analysis tool, other techniques like Scanning Electron Microscopy and Transmission Electron Microscopy can give complementary information on the morphology and local composition of the CRUD materials. Analysis of CRUD collected on BWR-reactor rods were realised with SEM in PSI. The morphology of the material, as well as the local composition was determined using imaging and Energy Dispersive X-Ray Spectroscopy (EDS) capabilities. The detailed analysis of the CRUD particles with SEM shows that the surface composition is not representative of the bulk composition of the material. Therefore the EDS technique can lead to erroneous composition determination. The paper presents the SEM and TEM measurement technique used and evaluates the capabilities and drawback of these methods for the analysis of CRUD material using the results obtained on BWR CRUD.

Keywords: CRUD, BWR, ICP-MS, SEM, TEM, X-Ray, EDS, Diffraction, SAD

Introduction

In this paper, we define the CRUD as the Fe-based deposit that is built on the outer cladding surface of the fuel rod in the nuclear reactor. In BWR with Zn injection, magnetic CRUD can be formed. This deposit on the cladding tube disturbs the non-destructive oxide thickness determination with standard eddy current measurement equipment. During the last years, new methods have been developed for the oxide thickness measurement in presence of magnetic CRUD. To apply these methods, some knowledge of the CRUD material is needed. Therefore PSI has started a detailed analysis of CRUD collected on BWR nuclear fuel rods. Due to the high radioactivity of the material, all the analyses have to be realised on dedicated instruments. The overall elemental composition and the isotopic distribution have been determined with ICP-MS (Inductively Coupled Plasma Mass Spectrometry), but this method gives no indication about the morphology, local composition and elemental distribution in the CRUD material. Therefore SEM (Scanning Electron Microscopy) has been used to determine the morphology and micro-composition of de CRUD. In addition, TEM (Transmission Electron Microscopy) has been applied to get very local element distribution in CRUD and some information on the crystallography of the material. This paper gives the results of preliminary analyses using these three analytical tools.

Specimen collection (sampling)

The CRUD material has been prepared / collected in two very different manners. Most of the analyses have been realised on CRUD material collected by scraping on filters (ICP-MS, SEM / EDS, TEM) and one analysis has been made on a cross section of a fuel rod prepared for metallographic analysis (SEM EDS mapping). The scraping of the rods was done in the nuclear power plant by grinding down a calibrated surface of the fuel rod under water in the spent fuel pool and filtering the CRUD containing Water through micropore filter membranes (polycarbonate). The CRUD-containing membranes have been stored in plastic boxes and sent to PSI without any further manipulation. The fuel rod cross section was made on a rod extracted during the same outage of the power plant as the one used for the CRUD scraping.

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Chemical composition of CRUD deposited material on filter by ICP-MS

Sample preparation

The CRUD loaded filter membranes have been weighted and dissolved in 5 ml H_2SO_4 (96%, suprapur, Merck) with addition of 5 ml H_2O_2 (30%, suprapur, Merck) by heating with IR-Light. After cooling down, 5 ml HF (48%, ultrapur, Merck) was added and heated again in a microwave oven. If the solution was not completely clear and colourless, 5 ml HNO_3 (65%, suprapur, Merck) was added to dissolve precipitates. The clear solution was diluted to about 50 ml with H_2O and weighted exactly to get a stock solution.

Analysis

The Analyses of three filter membranes have been realized with the shielded ICP-MS "PlasmaQuad 2+" (VG Elemental, Winsford, Cheshire, UK), installed in a 2 m^3 glove box. The analysis procedure is fully described in the document [1]. Due to the sampling method, the material collected on the filter is "contaminated" with the presence of other materials like ZrO_2 or material present in the reactor water. In order to be able to compare the CRUD composition determined by ICP-MS with the local measurement realised on CRUD particles, the data set has been reduced to only the standard CRUD forming elements: Cr, Mn, Fe, Co, Ni, Cu and Zn. The measurement of the oxygen content, which is a main constituent of the CRUD, is not possible as other materials present on the filter are also oxidised. Therefore the measured values for the elements Cr, Mn, Fe, Co, Ni, Cu and Zn normalised to 100% are given in the table 1 for the 3 filters. In the same table the average values as well as the standard deviation are calculated.

	1 Wt-%	2 Wt-%	3 Wt-%	Mean Wt-%	Stdv Wt-%
Cr	0.9	1.0	1.2	**1.0**	**0.1**
Mn	2.4	3.4	3.8	**3.2**	**0.6**
Fe	50.8	72.3	56.8	**60.0**	**9.1**
Co	0.7	0.4	0.3	**0.5**	**0.2**
Ni	3.2	5.6	6.7	**5.2**	**1.5**
Cu	0.2	0.1	0.0	**0.1**	**0.1**
Zn	41.9	17.3	31.3	**30.2**	**10.1**

Table 1 CRUD element composition (without O) measured by ICP-MS on three filters

Scanning Electron Microscopy of CRUD material deposited on filter

Sample preparation

A piece of the CRUD containing filter membranes has been fixed with conducting tape (Leit-C-Tab, Bal-Tec, Art. No. G3347) on a standard 12.5 mm sample holder and coated with Platinum by sputtering to reduce charging effects.

Instrument

The analyses have been realized with the PSI Hot-Laboratory SEM "Zeiss DSM 962", equipped with a standard Everhart-Thornley Secondary Electron Detector, a Robinson Backscattering Detector and the EDS-System "SIX" from Noran with the Pioneer Si(Li)-Detector (Norvar window).

Imaging

To determine the CRUD morphology and homogeneity, imaging has been done with secondary (SE) and backscattered (BSE) electrons. In spite of the metallic coating, electron-charging effects in the material make the observation of the material with SE impossible. With BSE, it was possible to acquire good quality pictures, but the presence of chemical inhomogeneity couldn't be determined due to the interfering topographic contrasts. The pictures presented in Fig. 1, show different particles deposited on the filter (background structure). Compact deposit layers are found as well as crystallites and more or less loose conglomerates, some of them built possibly during sampling in the water or on the filter membrane.
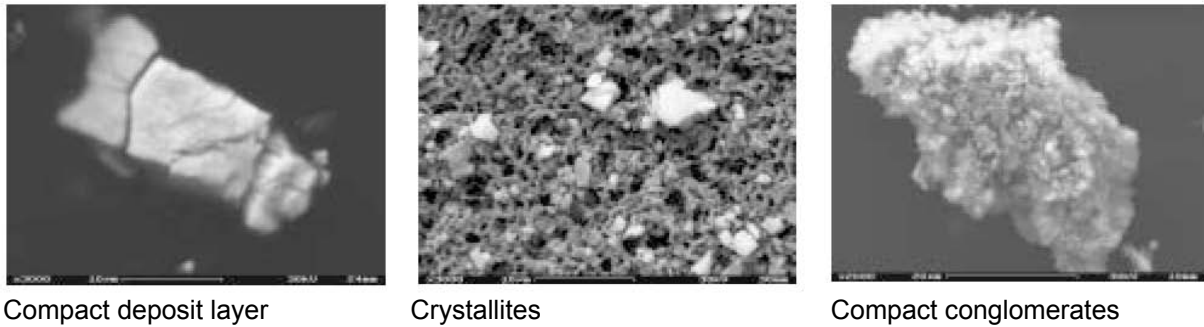
Compact deposit layer	Crystallites	Compact conglomerates

Fig. 1 Typical BSE images of CRUD material deposited on the filter

Energy dispersive X-Ray Spectroscopy (EDS)

Energy Dispersive X-Ray spectroscopy (EDS) analyses have been realised on different CRUD particles or agglomerates on the filter. These analyses give the local element composition at the surface of the CRUD particles (about 1 µm thick layer).
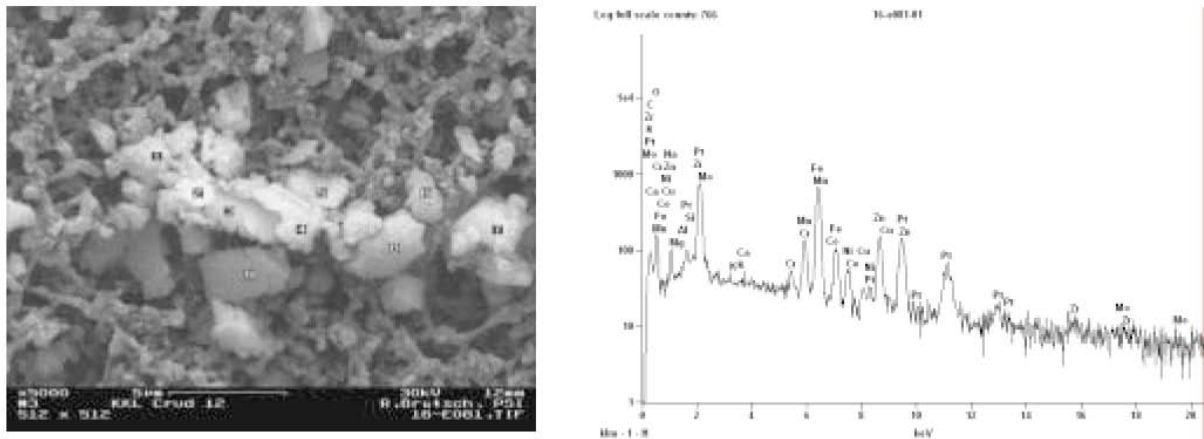
Fig. 2 Typical BSE image of the deposited material on the filter with the sampling of EDS measurements and an example of an EDS spectrum

	E03-1	E03-2	E03-3	E03-4	E03-5	E03-6	E03-7	E081-1	E081-2	E081-3	E081-4	E081-5	E081-6	E081-7	E081-8	E081-9	E021	E022	E023	Mean	Stdv.
	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%	Wt-%
Cr K	1.18	1.28	1.65	0.74	1.16	3.41	1.92	1.30	1.50	3.43	1.23	1.32	1.78	1.22	1.10	1.41	1.74	0.92	0.90	1.54	0.71
Mn K	10.20	8.50	20.31	5.35	6.44	5.25	15.24	9.66	10.39	21.47	11.91	9.53	12.39	7.73	8.27	17.54	11.62	5.07	7.68	10.77	4.70
Fe K	56.86	60.87	46.83	76.45	57.22	77.45	54.87	55.95	53.87	49.07	58.14	56.71	60.43	59.07	65.53	52.55	55.14	67.23	63.13	59.34	7.76
Co K	0.58	0.83	0.00	0.00	0.88	0.00	0.47	0.60	0.12	1.06	0.40	0.70	0.58	0.59	1.06	0.38	0.71	0.71	0.34	0.53	0.32
Ni K	6.22	5.95	6.34	3.15	7.48	4.20	6.51	5.25	7.86	2.02	6.89	7.69	5.06	8.74	5.61	3.89	5.32	6.19	5.64	5.79	1.63
Cu K	4.80	3.59	9.81	2.97	1.32	2.58	5.57	2.56	2.33	5.87	4.56	3.67	3.10	1.47	2.88	5.36	9.16	1.97	4.06	4.09	2.26
Zn K	20.15	18.99	15.07	11.34	25.50	7.10	15.42	24.67	23.94	17.08	16.88	20.38	16.65	21.17	15.55	18.88	16.30	17.92	18.25	17.96	4.29
Total	99.99	100.01	100.01	100.00	100.00	99.99	100.00	99.99	100.01	100.00	100.01	100.00	99.99	99.99	100.00	100.01	99.99	100.01	100.00	100.00	

Table 2 Measured local CRUD composition with EDS and mean and standard deviation of the measurements

An example of the measurement sampling and a typical EDS spectrum obtained on CRUD agglomerate is presented in Fig. 2. The main CRUD element concentrations determined by EDS on 19 CRUD particles or agglomerates are given in table 2 with the average value and standard deviation. The distribution of the main CRUD elements measured by EDS is in good agreement with the ICP-MS results, but the concentration of Zn is significant lesser whereas the concentrations of Cu and Mn are significant larger in the local EDS measurements.
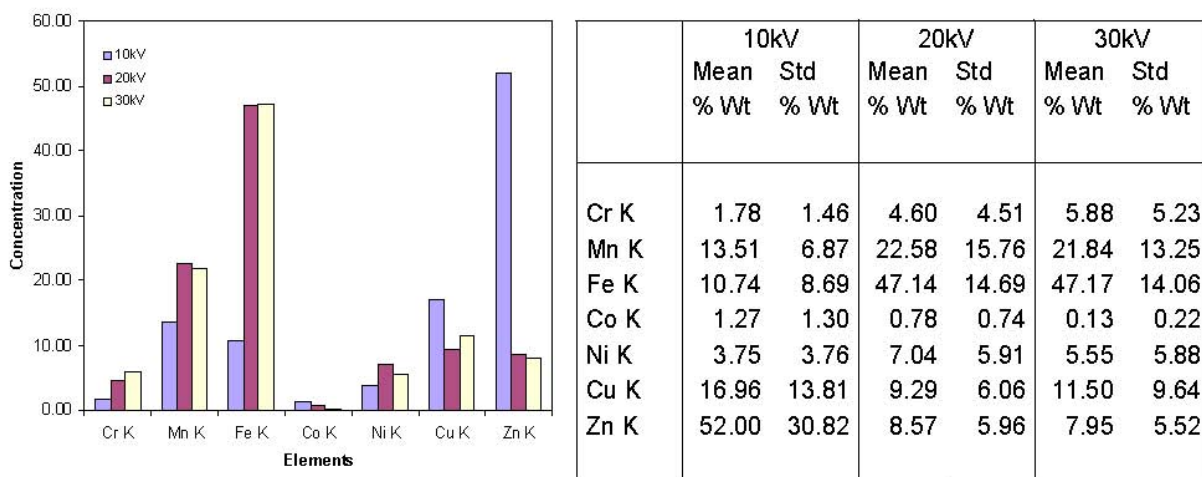

	10kV		20kV		30kV	
	Mean % Wt	Std % Wt	Mean % Wt	Std % Wt	Mean % Wt	Std % Wt
Cr K	1.78	1.46	4.60	4.51	5.88	5.23
Mn K	13.51	6.87	22.58	15.76	21.84	13.25
Fe K	10.74	8.69	47.14	14.69	47.17	14.06
Co K	1.27	1.30	0.78	0.74	0.13	0.22
Ni K	3.75	3.76	7.04	5.91	5.55	5.88
Cu K	16.96	13.81	9.29	6.06	11.50	9.64
Zn K	52.00	30.82	8.57	5.96	7.95	5.52

Fig. 3 Measured local CRUD composition with EDS in function of the energy voltage of the incident electron

The difference in the concentration determined by the two methods can result from different causes. One possibility is an inhomogeneous element distribution in the particles (larger or smaller concentration of some element at the surface of the particles). In order to clarify this observation, EDS measurement have been realised on some CRUD particles with different accelerating voltages for the incident electrons. This method allows changing the penetration range of the incident electrons and therefore the thickness of the analysed layer. The results are presented in Fig. 3. These analyses show a clear variation of some element concentration in function of the measurement depth. The concentration of Cr, Mn and Fe is clearly lesser at the surface of the particle than deep inside, the concentration of Co and Ni are relatively stable and finally the concentration of Cu and Zn are clearly larger at the surface of the particles. This is presented graphically in Fig. 3. These results demonstrate clearly that the element distribution in one CRUD particles is not homogeneous.

Scanning Electron Microscopy of CRUD on a fuel rod cross section

Sample preparation

A 5 mm long fuel piece was cut out of the fuel rod in PSI. After fuel extraction, the cladding material with the crud layer was embedded in epoxy resin and prepared for metallographic examination. The specimen was finally coated with Carbon prior to the SEM observation and analysis.

SEM / EDS element mapping

The CRUD material appears on the outer surface of the cladding as a quite porous layer. On this polished layer, EDS element mapping was realised to determine the qualitative element distribution inside the CRUD and gain information on the real homogeneity of the material (Fig. 4). The element mappings show that Fe, Co and Zn are mainly in the bulk CRUD material whereas Mn and Ni are on the surface of the material and finally Cu appears as precipitates (or artefacts from sample preparation). These measurements confirm the intrinsic inhomogeneity of the Crud material.

Transmission Electron Microscopy of CRUD material deposited on filter

Sample preparation

The CRUD material containing filter membrane has been dissolved in Acetone and then the deposit was precipitated. Two times the clear Acetone phase has been removed with a pipette and pure Acetone was added again to wash out the dissolved polycarbonate from the filter to get pure CRUD deposit material.

With $KAl(SO_4)_2 \cdot 12H_2O$ (Potassium alaun) some bigger crystals have been grew in a saturated (65ºC) solution. The crystals have been coated with carbon. Then with a pipette a drop of CRUD containing Acetone was deposited on the coated crystal and another layer of carbon was deposited to create a Carbon-CRUD-Carbon-Sandwich. Then the Crystal was dropped into a 1:1 H_2O-Ethanol-Solution and the CRUD containing carbon layers have been collected on a TEM grid.
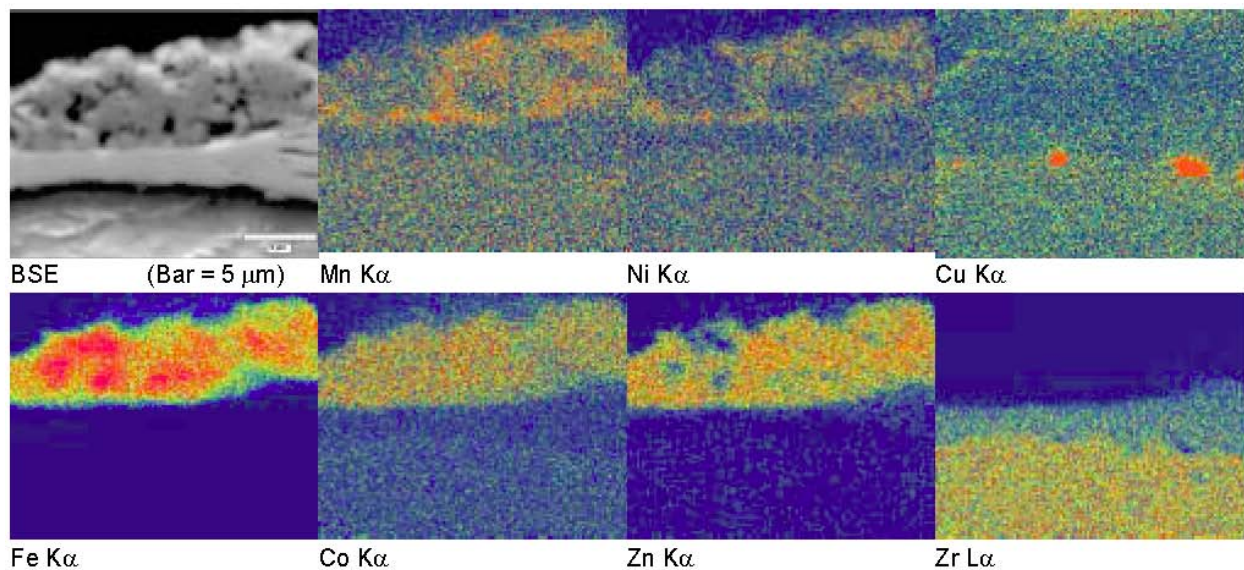

Fig. 4 Element mapping in CRUD measured by EDS on a fuel rod cross section

Imaging, Energy dispersive X-Ray Analysis, Electron Diffraction

The TEM analyses have been done with a JEOL 2010 Electron Microscope, equipped with a Link® EDS system. Very few particles or agglomerate collected on the carbon foil were thin enough to be transparent. Nevertheless it was possible to collect images, EDS analyses and Selected Area Diffractions (SAD) on few Fe based particles. Most of the SADs show a superposition of different diffraction pattern indicating the presence of different crystal orientation and / or phases in the beam. This indicates that the particles analysed are probably agglomerates of very thin particles. Preliminary analyses of some of these SAD indicate the presence of hematite and probably of magnetite or spinel (FeMnZn) Fe_xO_4. But most of the pattern cannot be indexed and this first analysis must be confirmed by further studies (Fig. 5). Analyses realised on two particles are presented in Fig. 6. The results demonstrate the presence of material with almost no Zn and low Mn content on the side of other with a Zn and Mn content up to 13% Wt. This is also a confirmation of the highly inhomogeneous local composition of the CRUD.
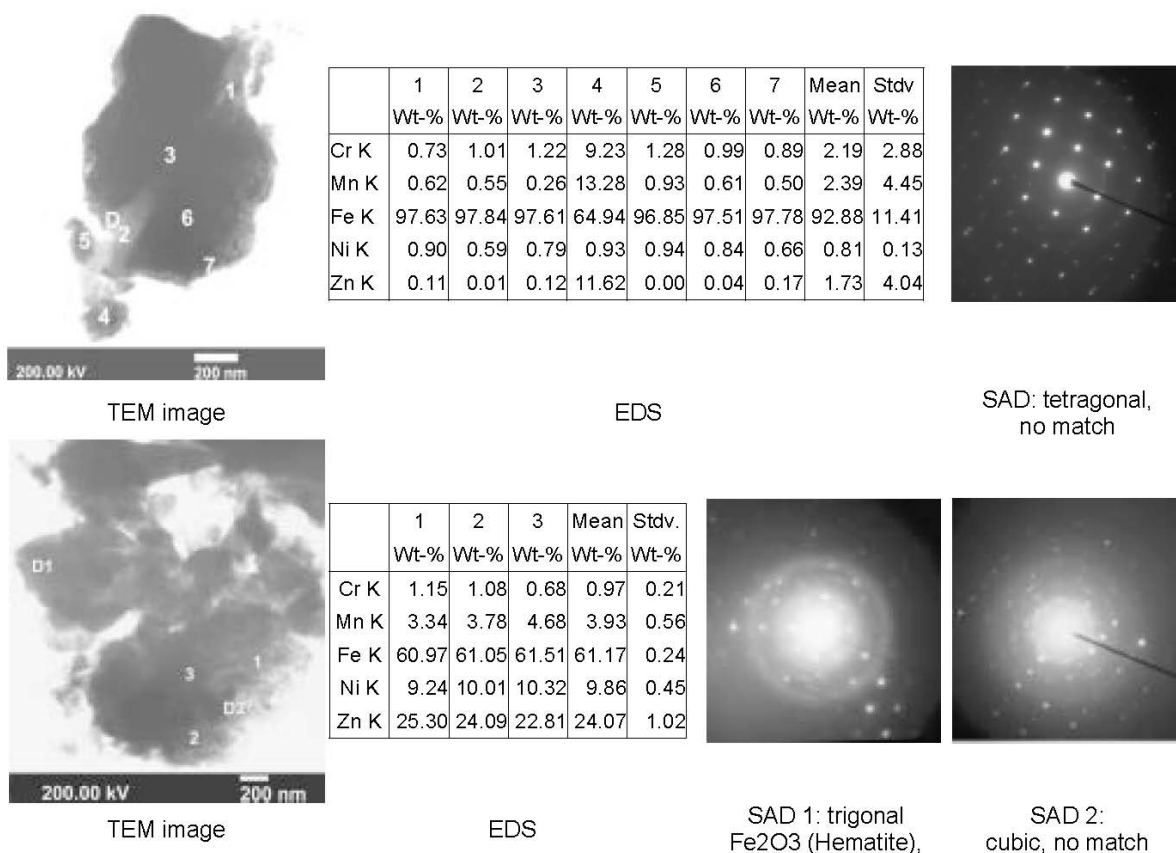

	1 Wt-%	2 Wt-%	3 Wt-%	4 Wt-%	5 Wt-%	6 Wt-%	7 Wt-%	Mean Wt-%	Stdv Wt-%
Cr K	0.73	1.01	1.22	9.23	1.28	0.99	0.89	2.19	2.88
Mn K	0.62	0.55	0.26	13.28	0.93	0.61	0.50	2.39	4.45
Fe K	97.63	97.84	97.61	64.94	96.85	97.51	97.78	92.88	11.41
Ni K	0.90	0.59	0.79	0.93	0.94	0.84	0.66	0.81	0.13
Zn K	0.11	0.01	0.12	11.62	0.00	0.04	0.17	1.73	4.04

TEM image   EDS   SAD: tetragonal, no match

	1 Wt-%	2 Wt-%	3 Wt-%	Mean Wt-%	Stdv. Wt-%
Cr K	1.15	1.08	0.68	0.97	0.21
Mn K	3.34	3.78	4.68	3.93	0.56
Fe K	60.97	61.05	61.51	61.17	0.24
Ni K	9.24	10.01	10.32	9.86	0.45
Zn K	25.30	24.09	22.81	24.07	1.02

TEM image   EDS   SAD 1: trigonal Fe2O3 (Hematite),   SAD 2: cubic, no match

Fig. 5 TEM bright field images, EDS analyses and SAD pattern

Discussion

The comparison between the global and local measurement of the CRUD composition show variation that can be explained by an inhomogeneous element distribution in the CRUD material itself. The SEM detailed analyses show a surface composition different from the bulk composition of the CRUD particles or agglomerate and the TEM analyses demonstrate the superposition of different phases at a very small spatial scale. Therefore, this study shows an intrinsic difficulty for the analysis of the physical properties and morphology of the CRUD material. Due to the very high inhomogeneity of the CRUD, the use of the high spatial resolution analytic techniques as SEM or TEM can deliver misleading information. It must be noted that the material sampling technique used for most of the analysis presented in this paper (scraping) is well suited for the determination of the global composition of the material (ICP-MS) but far to be perfect for the SEM or TEM analyse as the original material is grinded down to a very thin powder. This could have an influence on its local structure, composition and homogeneity. For more detailed analysis of the CRUD material new sampling procedures should be developed.

Conclusions

SEM and TEM are complementary methods to ICP-MS and can give interesting additional information by the analysis of CRUD material. ICP-MS gives accurate but global values for the element concentration in CRUD material whereas SEM and TEM give very local information about the morphology, element concentration, homogeneity and structure of single particles and conglomerates. The SEM analyses show that CRUD deposit can appear as a compact deposit layer or as more or less loose conglomerates and crystallites. The mean element concentration of Cr, Co, Fe and Ni is similar to the ICP-MS results whereas the concentration of Zn is significant less and that one from Mn and Cu significant higher in EDS. TEM deliver very local elemental analyses in single particles and information on its structure. The quality of the sample preparation is instrumental in order to obtain good analysis. The study has shown the potential and danger of applying local analytical analysis techniques like SEM and TEM to the determination of the CRUD structure and composition. The development of less abrasive material sampling would increase the interest of these analytical techniques.

References

[1]   PSI AW-43-98-18, Rev. 0: Quantitative Elementanalyse mittels ICP-MS; Ines Leopold, 13.08.98 (internal documentation)