

Synthesis and dissolution of model corrosion compounds in testing of novel decontamination medium

Martin Strejc

ÚJV Řež, a. s.

Hlavní 130, Husinec, 250 68, Czech Republic

martin.strejc@ujv.cz

Kateřina Čubová¹, Mojmír Němec¹

¹ CTU in Prague, Břehová 7, Praha 1, 115 19, Czech Republic

mojmir.nemec@fjfi.cvut.cz, katerina.cubova@fjfi.cvut.cz,

Radek Trtílek²

² ÚJV Řež a. s., Hlavní 130, Husinec, 250 68, Czech Republic

radek.trtilek@ujv.cz

ABSTRACT

During operation of each nuclear power plant, a corrosion layer forms on the inner surfaces of the primary circuit. The application of a suitable decontamination medium capable of removing these layers with the possibility of regeneration of its active components would allow the reduction of the total volume of radioactive waste. This work is focused on the development of model corrosion layer compounds to simulating real layers arising during the operation of the nuclear power plant followed by dissolution of the layer using the new developed decontamination medium.

INTRODUCTION

Except the reactor, the most contaminated part of the VVER nuclear power plant is the primary circuit, where radionuclides are accumulated on its inner surface adsorbed and incorporated in the corrosion layers. Usually, these layers are partially dissolved and modified during regular decontamination, however it results in gradual built-up of the corrosion layers and their in-growth to the construction material. Due to operation history and related changes in chemistry conditions during operation, a complex multilayer structure of primary circuit corrosion layers was found [1, 2]. Simplified, the iron hydroxide layer was located on the top-surface followed by durable and chemically resistant spinel or spinel-like structures based on chrome-nickel-iron composition. Chrome-nickel austenitic phase was identified as the deepest structure incorporated to the construction steel. Actual composition of individual layers is specific for each nuclear power plant and its operational history. The main challenge of the decontamination process – operational or during decommissioning – seems to be the chemical stability and low solubility of the chrome-nickel-iron spinel materials oxide [3, 4, 5].

Synthesis of a corrosion compounds with a structure as close as possible to the composition of a real corrosion layer with the respective amount of chromium was one of the main goals of this work followed by dissolution of the layer using new developed decontamination medium.

RESULTS

The procedure of preparation of spinel-based materials and their dissolution using recyclable decontamination medium based on persulfates is described in the following chapters. The developed solution belongs to the group of oxidizing decontamination media, where the oxidation compound is persulfate in acidic environment. Due to actual patent pending no closer details about the decontamination solution may be provided.

MODEL CORROSION COMPOUNDS SYNTHESIS

As it is mentioned in the introduction, real corrosion layers with spinel-structured materials with higher amount of chromium show high resistance to dissolution. Unfortunately, the real construction material of the primary circuit with operational history and with a developed corrosion layer was and is not easily available for testing. For this reason the synthesis of simulant materials with properties similar to the real corrosion layer had to be prepared.

A method of preparation of spinel-like materials based on sintering principle was developed. Metal oxides were used as precursors for this method using high temperature sintering of well-homogenized mixtures. Metal oxides were homogenized by a ball mill. XRD a SEM-EDX were used as the analytical methods to identify composition of spinel materials. An example of XRD analysis is shown on Figure 1.

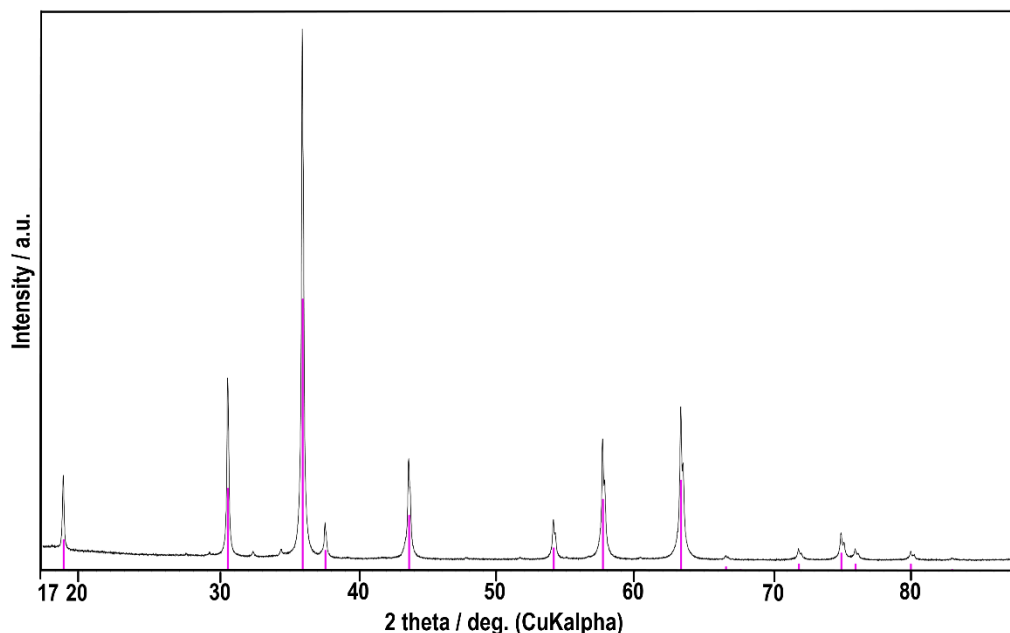


Figure 1: XRD spectra of the sample V17, lines of the identified library compound are highlighted.

In total about 25 testing samples of model materials were prepared, five of them (Table 1) were selected for dissolution testing to cover wide potential composition of possible corrosion layers.

Table 1: Composition of selected mixed materials [wt. %] prepared by high temperature sintering and used for dissolution testing.

	V11	V13	V17	V20	V24
Cr_2O_3	26,7	30,0	–	–	11,7
Fe_2O_3	33,3	29,3	–	–	–
Fe_2NiO_4	40,0	40,7	–	–	–
$\text{Cr}_{0,4}\text{Fe}_{1,6}\text{NiO}_4$	–	–	–	–	73,6
$\text{Cr}_{1,6}\text{Fe}_{0,4}\text{O}_3$	–	–	–	–	14,8
$\text{Cr}_2\text{Fe}_2\text{Ni}_2\text{O}_3$	–	–	100	–	–
$\text{Cr}_{0,9}\text{Fe}_{2,8}\text{Ni}_{2,4}\text{Mn}_{1,6}\text{O}_3$	–	–	–	100	–

DISSOLUTION TEST OF SELECTED MODEL CORROSION PRODUCTS

Several sets of experiments were performed to test the solubility of the model materials – the composition of the selected materials is listed in the Table 1 above.

Recyclable decontamination medium based on persulfates and developed at Department of nuclear chemistry, CTU in Prague, was tested for this purpose. The experiments were carried on at two different temperatures (50 °C and 80 °C) for five hours. The samples were analysed by AAS (Atomic Absorption Spectroscopy) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) measurement. Results obtained are shown in the Figure 2.

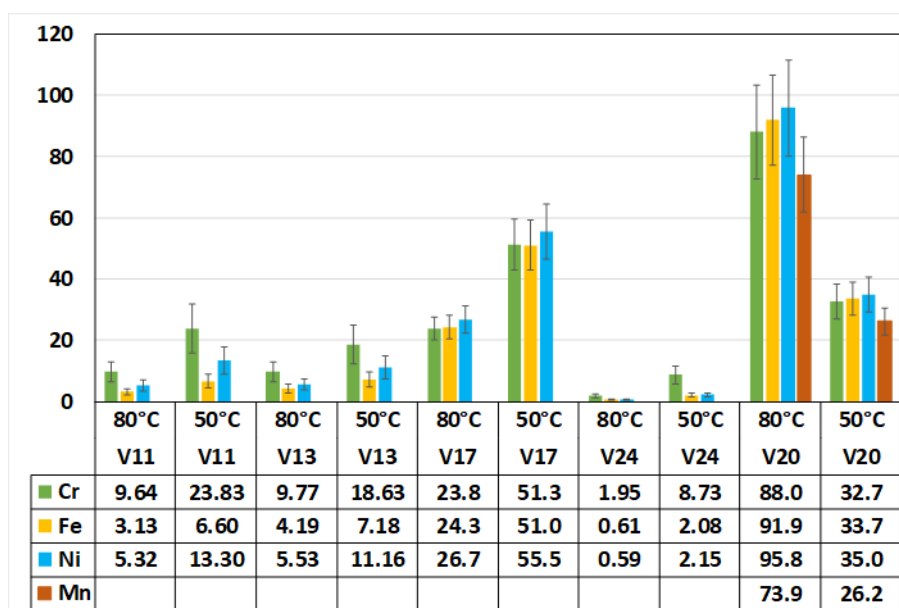


Figure 2: Dissolution of the model materials in the proposed decontamination solution after 5 contact hours and 400 cm³/g V/m in the ratio (% , numbers and Y-axis) of the initial content of the respective metal

It was found out that substrate composition and temperature play a major role. The obtained results show the highest efficiency of the decontamination medium in samples V17 and V20, whose composition are close to the real corrosion layer. The data also show that the abundance of chromium and its structural role in the compound play a main role in the resistivity of the material to oxidative dissolution. This is in agreement with literature data [6, 7].

From the experiments performed two main conclusions followed:

- In the materials with Fe, Ni or Mn as the major components, the solubility increases with increasing temperature.
- Materials with higher chromium content are dissolving more at lower temperature (50°C).

SUMMARY AND CONCLUSIONS

Procedure for the preparation of a simulated corrosion layer was developed, composition corresponds to the corrosion layer of the primary circuit VVER 440. The obtained samples of the simulated corrosion layer were analysed by XRD and SEM-EDX.

The method of synthesis of the model corrosion layer from the starting materials proved to be promising, which, in contrast to the significantly slower method of growing such a layer, allows to create a sufficient amount of sample in a reasonable time.

The dissolution of the material with a composition very close to the real corrosion layer, which occurs in the primary circuit of VVER units was successfully tested.

In the real decontamination procedure even a partial disruption of the corrosion layer is sufficient. From this point of view, the decontamination solution can be considered as sufficiently effective.

REFERENCES

- [1] Varga, K.; Németh, Z.; Szabó, A.; Radó, K.; Oravetz, D.; Homonnay, Z.; Schunk, J.; Tilky, P.; Körösi, F., Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators. Part I. General corrosion state and morphology. *Journal of Nuclear Materials* **2006**, *348* (1), 181-190.
- [2] Lore Homonnay, Z.; Kuzmann, E.; Varga, K.; Németh, Z.; Szabó, A.; Radó, K.; Makó, K. É.; Kövér, L.; Cserny, I.; Varga, D.; Tóth, J.; Schunk, J.; Tilky, P.; Patek, G., Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators. Part II. Chemical composition and structure of tube surfaces. *Journal of Nuclear Materials* **2006**, *348* (1), 191-204.
- [3] Szabó, A.; Varga, K.; Németh, Z.; Radó, K.; Oravetz, D.; Makó, K. É.; Homonnay, Z.; Kuzmann, E.; Tilky, P.; Schunk, J.; Patek, G., Effect of a chemical decontamination procedure on the corrosion state of the heat exchanger tubes of steam generators. *Corrosion Science*, 2006, *48* (9), 2727–2749.
- [4] Grygar, T.; Zmitko, M., Corrosion products behaviour under VVER primary coolant conditions. Chemistry 2002: International conference on water chemistry in nuclear reactors systems - operation optimisation and new developments, France, 2002.
- [5] Zmitko, M.; Kysela, J., Coolant technology and experience in VVER units. *Power Plant Chemistry*, 2005, *7*(3), 133–141.
- [6] Kysela, J.; Zmitko, M.; Yurmanov, V. A.; Tiapkov, V. F., Primary coolant chemistry in VVER units. *Nuclear Engineering and Design*, 1996, *160* (1), 185-192.
- [7] Katona, T., Long-Term Operation of VVER Power Plants. 2011.