

## PROTECTIVE COATING AND ITS INFLUENCE ON CORROSION BEHAVIOR OF METAL CONTAINERS FOR HIGH-LEVEL WASTE IMMOBILISATION

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*The article explores nickel-based protective coatings and their influence on high-temperature changes occurring on the inner surface of steel containers designed for HLW immobilization provided their interaction with the melts of model waste form materials. It evaluates the corrosion behavior of container surfaces with a nickel-based protective coating depending on its application method, i.e., galvanic and chemical. The study indicates the factors governing the corrosion depth, i. e., the depth to which the container steel surface may get altered depending on 4 different waste form material compositions. The study demonstrates high efficiency of the galvanic method in terms of nickel-based protective coating application and the major influence that high sodium and calcium content has on the depth of corrosion penetration into container surface.*

**Keywords:** radioactive waste, immobilization, borosilicate waste form materials, steel container, corrosion.

### Introduction

In keeping with the basic flowchart for high-level waste (HLW) immobilization via the vitrification method, the final stage of this process involves a melt of a waste form material (glass mass) that is poured into steel containers [1]–[3]. The high-temperature surface interaction occurring along the way is accompanied by their corrosion and mutual component diffusion in the contact zone [4], [9], [10]. This intense and prolonged interaction between steel – waste form melt and HLW occurs inside the electric furnace, namely, within the area fitted with electrodes, affecting their state and service life in a quite considerable way. Moreover, when the waste form melt with the HLW is poured, such interaction drives changes in the inner container surface, which may affect container integrity at the storage stage.

Therefore, these processes causing electrode and container surface degradation should be slowed

down to the extent possible to extend their service life, which explains the relevance of the measures proposed to mitigate the high-temperature corrosion and arises great interest in material interactions and their experimental studies.

Previous experimental studies focused on high-temperature interaction of nickel-chromium-containing steel grades with borosilicate melts simulating HLW waste form materials have revealed intensive elemental exchange in the melt/metal zone [5], [6]. The multicomponent diffusion processes contributed to uneven dissolution of steel components in the waste form borosilicate melt [7]–[10].

Depending on its chemical composition, there are two options for the contact layer structure that may emerge on the surface and slow down the rate of steel component dissolution [9], [10]. The first option suggests that the entire nickel inventory is

concentrated in the form of a thin protective metal film, whereas iron, chromium and manganese would form a separate porous coating of spinel crystals filled with borosilicate material. Under the second option, an aggregate wide porous layer of metallic nickel and iron-chromium spinel grains also filled with borosilicate material was formed.

The study evidences the protective nature of the resulting metallic nickel layer and indicates high performance of steel grades and alloys high in nickel as potential container materials for HLW immobilization. Less costly method contributing to less intensive high-temperature corrosion provides for some additional protective coatings applied to the inner surface. Depending on their composition, the applied method and the coating thickness, one may considerably reduce the melt impact, slow down the corrosion processes evolving on the surface of containers filled with HLW waste form materials and extend their safe storage time.

A study was launched to investigate the ways contributing to more effective application of protective nickel coatings assuming their interaction with the waste form melt material under the HLW vitrification process. Under this study, findings on high-temperature steel surface corrosion processes evolving in the contact zone with four model aluminoborosilicate melts of different compositions have been compared considering the above film deposited by galvanic and chemical (electroless) methods.

Experimental part

Under this study, sample compositions of model waste form materials constituting to the borosilicate system  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{B}_2\text{O}_3-\text{SiO}_2$  have been selected from a range of analytical-reagent grade  $\text{SiO}_2$ , high purity  $\text{B}_2\text{O}_3$  and reagent-grade  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . The content of components in the initial mixtures (Table 1) was selected considering data on average chemical composition of waste form materials used for HLW immobilization purposes [11]–[13] and reflects different boron content and alkaline/alkaline earth cation (Na/Ca) ratios.

Table 1. Initial compositions of waste form glasses according to their synthesis

Sample	Content, mol. %					
	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{TiO}_2$	$\text{B}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$
1-NCBS	20	10	2	16	5	47
3-NCBS	30	-	2	16	5	47
4-NCBS	28	10	2	8	5	47
6-NCBS	38	-	2	8	5	47

Pre-treated component mixtures were melted in platinum crucibles at 1,200–1,250 °C and the resulting melt was cooled rapidly (quenching) according to a method described in [14]–[17]. This process resulted in waste form material samples: transparent and macroscopically homogeneous ingots of an irregular shape weighing 5–10 g.

Mini-containers have been manufactured from alloyed corrosion-resistant, heat- and flame-resistant chromium-nickel steel grade 08Kh18N10 (AISI 304H) selected for the study: 12 mm high cylinders were cut from a steel rod ( $\varnothing$  14 mm), the centers of which were penetrated by blind 6 mm deep holes with a diameter of 6 mm. Their internal walls were grinded and polished resulting in a smoothest surface. Protective nickel coatings were applied to the polished steel surface of the manufactured mini-containers. The coatings were applied either by galvanic or electroless methods. Under the first method, a nickel layer was deposited on the inner container walls under an electric current ( $U=4$  V) applied for 30 minutes using the Watts sulfate electrolyte. The steel surface with the applied protective layer had a characteristic matte gray color (Figure 1).

It took one hour to implement the electroless nickel plating, which was done at a temperature of 97 °C using a  $\text{NiCl}_2 \times 6\text{H}_2\text{O}$   $\text{CH}_3\text{COONa} \times 3\text{H}_2\text{O}$   $\text{NaPH}_2\text{O}_2 \times \text{H}_2\text{O}$  solution ( $21 \times 10 \times 24$  g/L, pH 5.2). Due to sodium hypophosphite applied under this method, phosphorus accounted for a protective layer component, which, on the one hand, resulted in higher mechanical strength and wear resistance of the applied layer, and on the other hand, made it less stable under chemical and temperature impacts. The resulting coating had a yellowish-white color with a slight shine (Figure 1) and the following chemical composition: 95 % wt. Ni and 5 % wt. P.

Under high-temperature studies, crushed waste form material of an equal mass ( $0.45 \pm 0.01$ ) g was poured into coated mini-containers. Loaded containers were installed into an electric furnace preheated

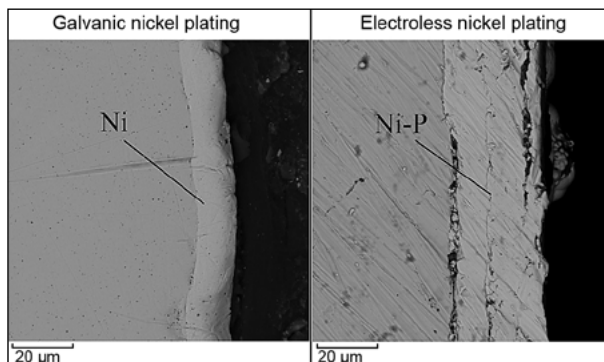


Figure 1. Appearance of a container wall with a protective coating applied by galvanic and electroless nickel plating methods

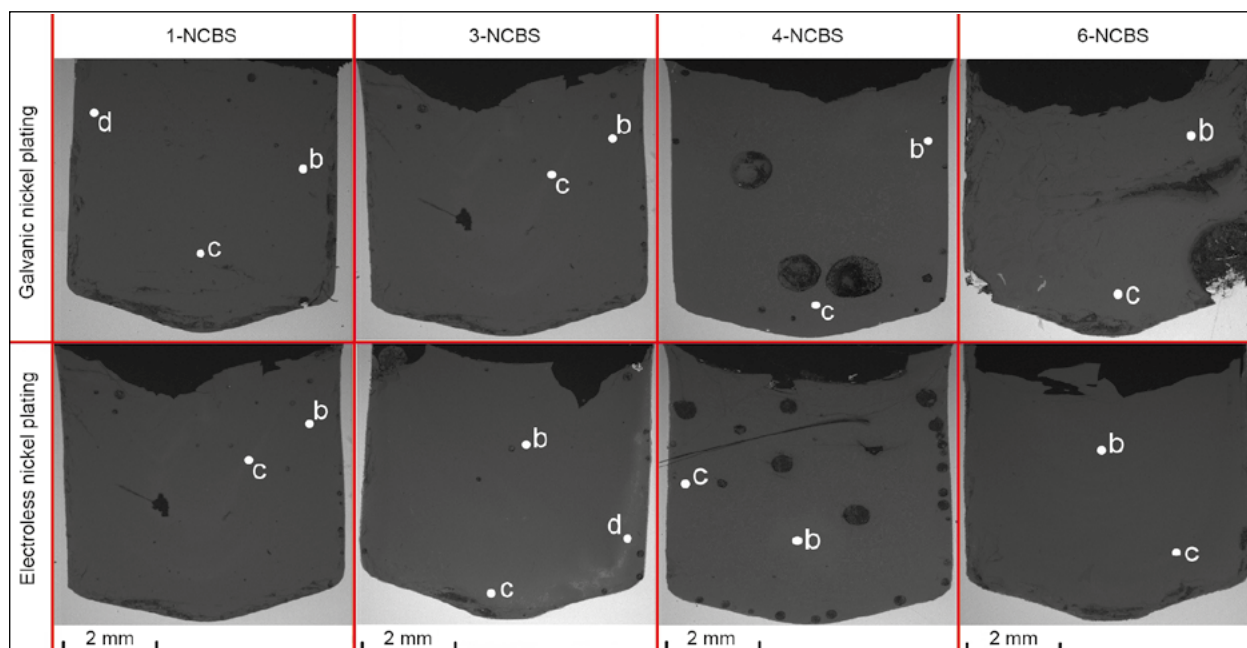


Figure 2. Appearance of containers with nickel plating applied by galvanic and electroless methods upon completing the high temperature experiment. Light areas correspond to metal, dark areas correspond to borosilicate glass

to a temperature of 800 °C, which was subsequently increased to 1,300 °C at a rate of 5 °/min. They were kept at this maximum temperature for 60 minutes and then removed and placed into a second furnace preheated to 400 °C. After container reloading, the second furnace was turned off and slowly cooled to room temperature with the containers remaining inside. At the next stage, the containers were removed from the electric furnace and cut together with the waste form material contained inside. The cutting was performed along a vertical plane passing through the middle of the recess. The surface of the resulting section was ground, polished and prepared for microscopic examination (Figure 2).

The resulting polished sections (specimens) have been investigated using a Tescan Vega 3 Sbu scanning electron microscope and an energy-dispersive spectrometer Oxford Instruments X-act (Oxford Instruments, UK). The study provided data on the surface layer of the container material and aluminoborosilicate waste form materials, namely, its chemical composition in the high-temperature contact interaction zone. All of these findings are presented in Figures 3–8 and in Tables 2–4.

## Findings

### Galvanic nickel plating

The left side in Figure 1 shows a pronounced 6–8 μm thick nickel layer emerged upon completing the galvanic nickel plating process observed in back-scattered electrons (BSE) on the mini-container surfaces along all of the container walls. Steel container

surfaces altered due to high-temperature interaction with the waste form melt have been investigated: a film of mixed composition (Ni, Fe) (Fe, Cr)<sub>2</sub>O<sub>4</sub> have emerged in the contact zone running parallel to this layer. Due to the mutual diffusion occurring between the steel components and the waste form melt, this film was found being partially filled with the waste form material (Figure 3).

The minimum thickness of these contact layers was observed in the 1-NCBS. 3-NCBS, 4-NCBS and 6-NCBS samples revealed partial separation of the layer being high in nickel from the steel container surface, as well as chromium and iron oxide film thickening. Gas bubbles observed in the solidified waste form material (glass) could be explained by CO generation driven by the oxidation carbon released from the steel. Nickel was observed in these gas bubbles: it was captured from the protective layer causing no oxidizing effect. In 3-NCBS, 4-NCBS and 6-NCBS samples, small amounts of dissolved iron unevenly distributed throughout the glass volume were found in the waste form material (Table 2).

Table 2. Average composition of the waste form glass in the studied spots after completing the galvanic nickel plating process (Figure 2)

Sample	Composition								
	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	NiO	B <sub>2</sub> O <sub>3</sub>
1-NCBS	13.5	6.1	46.9	11.5	2.2	-	0.2	-	19.3
3-NCBS	16.3	5.6	44.3	-	2.1	0.1	1.9	-	29.4
4-NCBS	16.1	5.5	42.6	8.1	2.4	-	4.6	0.2	20.2
6-NCBS	16.1	3.6	28.0	-	2.3	-	1.6	0.3	47.8

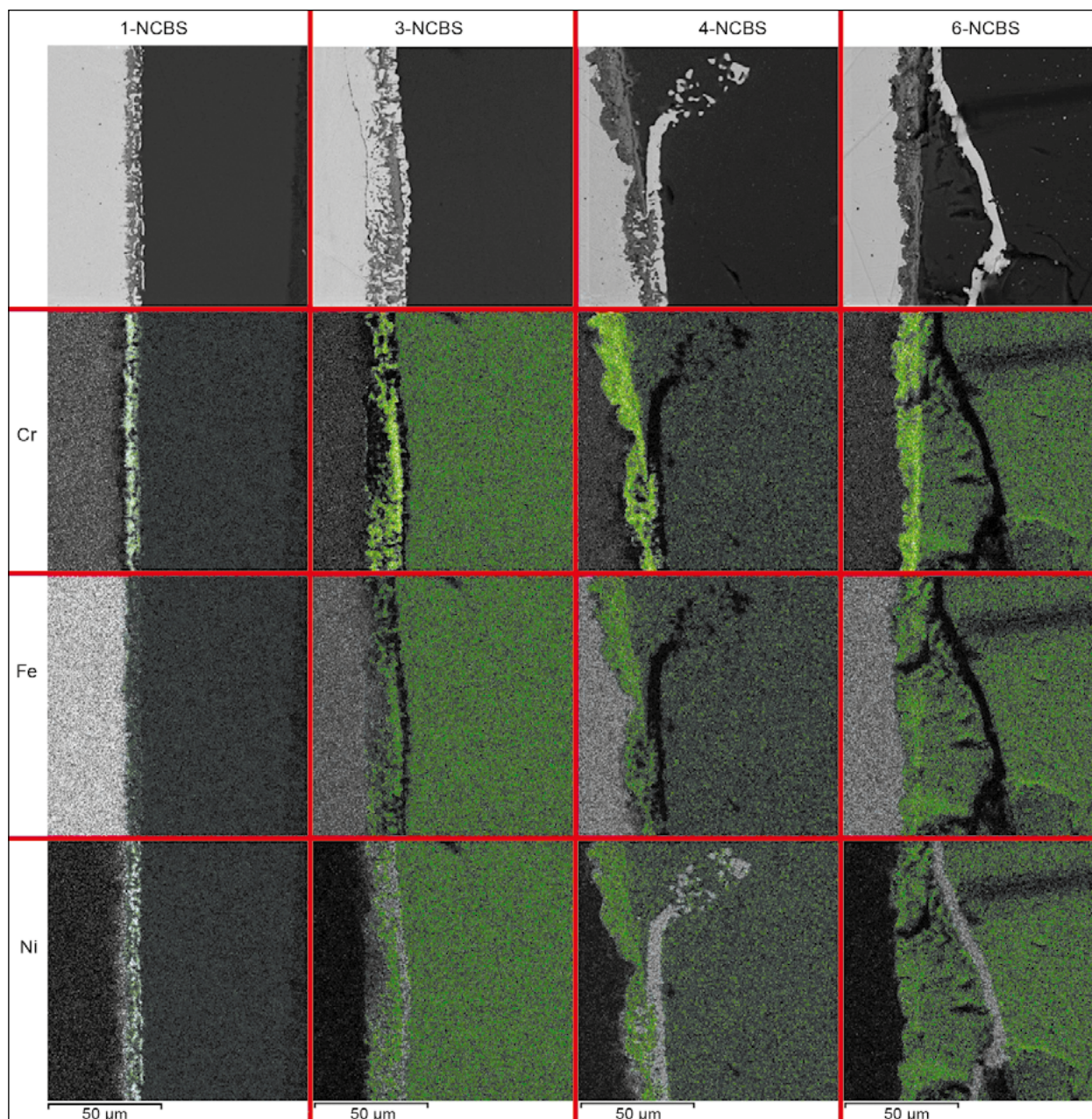


Figure 3. Contact zone of waste form glass with the surface of containers and their protective film upon applying the galvanic nickel plating (oxygen is indicated in green)

### Electroless nickel plating

Electroless nickel plating resulted in up to 18 microns thick uniform film containing nickel and phosphorus that emerged on the inner container surfaces (Figure 1, right). High-temperature interaction with the waste form melt on the walls of these mini-containers resulted in its detachment with a wide porous layer of mixed chromium and iron oxides formed in the glass volume. Two areas of phosphorus concentration were observed: separate narrow areas directly in the porous layer of all samples and the bulk of the waste form material, namely, in the spots high in calcium, only in case

of compositions with calcium-containing waste form material (1-NCBS and 4-NCBS) (Figure 4).

Similarly to galvanic nickel plating, the minimum thickness of this layer and the minimal iron and chromium entrainment into glass waste form volume was observed in case of the 1-NCBS material composition (Figure 4, Table 3). Samples with 3-NCBS and 6-NCBS material revealed highly modified and altered zone of their contact with the steel. The widest area of interaction with high material entrainment was observed in the 4-NCBS sample. All nickel inventory released into the waste form volume has remained unoxidized.

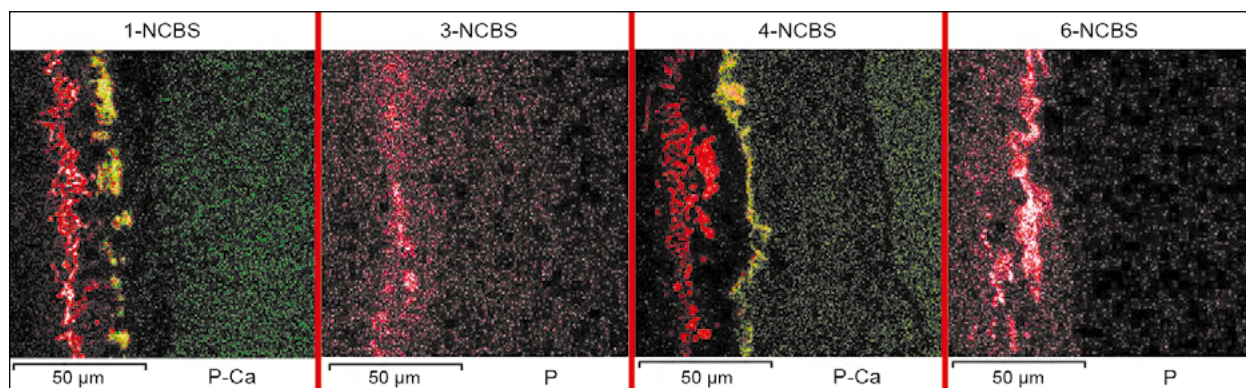


Figure 4. Distribution of calcium and phosphorus in the contact layer of solidified calcium-containing waste material in mini-containers upon completing the nickel plating process, red color – P, green color – Ca

**Table 3. Average composition of waste form glass upon completing the electroless nickel plating at the studied points (Figure 2)**

Sample	Composition								
	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	NiO	B <sub>2</sub> O <sub>3</sub>
1-NCBS	16.5	6	45.9	11.7	2.1	0.1	1.4	-	16.1
3-NCBS	14.8	5.3	41	-	2	-	7.8	0.1	28.7
4-NCBS	18.4	5.2	40	9.4	2.4	0.1	4.5	0.3	19.4
6-NCBS	26.8	5.5	43.1	-	2.5	0.2	2.6	-	19.1

## Discussion

Irrespective of the method implemented to apply the protective nickel film, the 1-NCBS sample accounted for the minimal interaction zone between the container and the waste form glass: on average 9 µm and 19 µm in case galvanic and electroless methods respectively (Figures 3 and 5). The zone of corrosion product entrainment from the container surface into the waste form volume averaged 20 and 40 µm, respectively. Another specific feature revealed for the 1-NCBS sample composition under this study was the minimal, compared to others, content of alkaline elements (sodium) in it contributing to its high melt viscosity [10], [18].

Irrespective of the method implemented to apply the protective nickel film, the 3-NCBS sample had a wider interface between the container and the waste form glass. Under galvanic nickel plating, the corrosion zone averaged 18 microns with occasional nickel layer detachment from the container surface. Under the electroless method, it averaged 38 microns with chromium oxide entrainment from the container surface deep into the glass amounting to up to 75 microns. Notable corrosion zone extension was promoted by higher alkaline element content and, correspondingly, lower melt viscosity [10], [18].

For the same reason, higher content of iron oxides could be observed in the glass volume.

The corrosion zone resulted from galvanic nickel plating in containers with the 4-NCBS waste form glass averaged 15 microns, whereas an altered material section extending up to 60 microns deep was formed upon completing the high-temperature experiment and applying the electroless plating method. A residual area being about 27 microns thick and enriched with phosphorus was observed in this case on the container wall. Notable degradation of the applied protective film and a wide zone involving oxide mixtures of all steel components, waste form material and phosphorus could be explained by the high content of alkali metal and the negative impact produced by calcium. Both plating methods resulted in the detachment of the protective nickel layer from the surface with some oxidized iron found in the glass volume.

Containers with a protective film produced by the galvanic nickel plating method and the 6-NCBS material had a corrosion zone averaging some 11 microns. Notable detachment of the protective layer was identified with some individual nickel particles entrained into the glass volume to a depth of 45 microns. Electroless plating also contributed to high dilution of the contact zone with the waste form melt observed to a depth of 37 µm accompanied by container material detachment and entrainment into the glass volume to a depth of 60 µm. Based on its chemical composition, the 6-NCBS waste form melt had the lowest viscosity compared to all of the studied samples.

## Conclusion

Galvanic nickel plating applied to the container surfaces, namely, the containers intended for HLW immobilization with waste form materials is seen as a most effective technique improving their corrosion resistance. Corrosion zone was compared

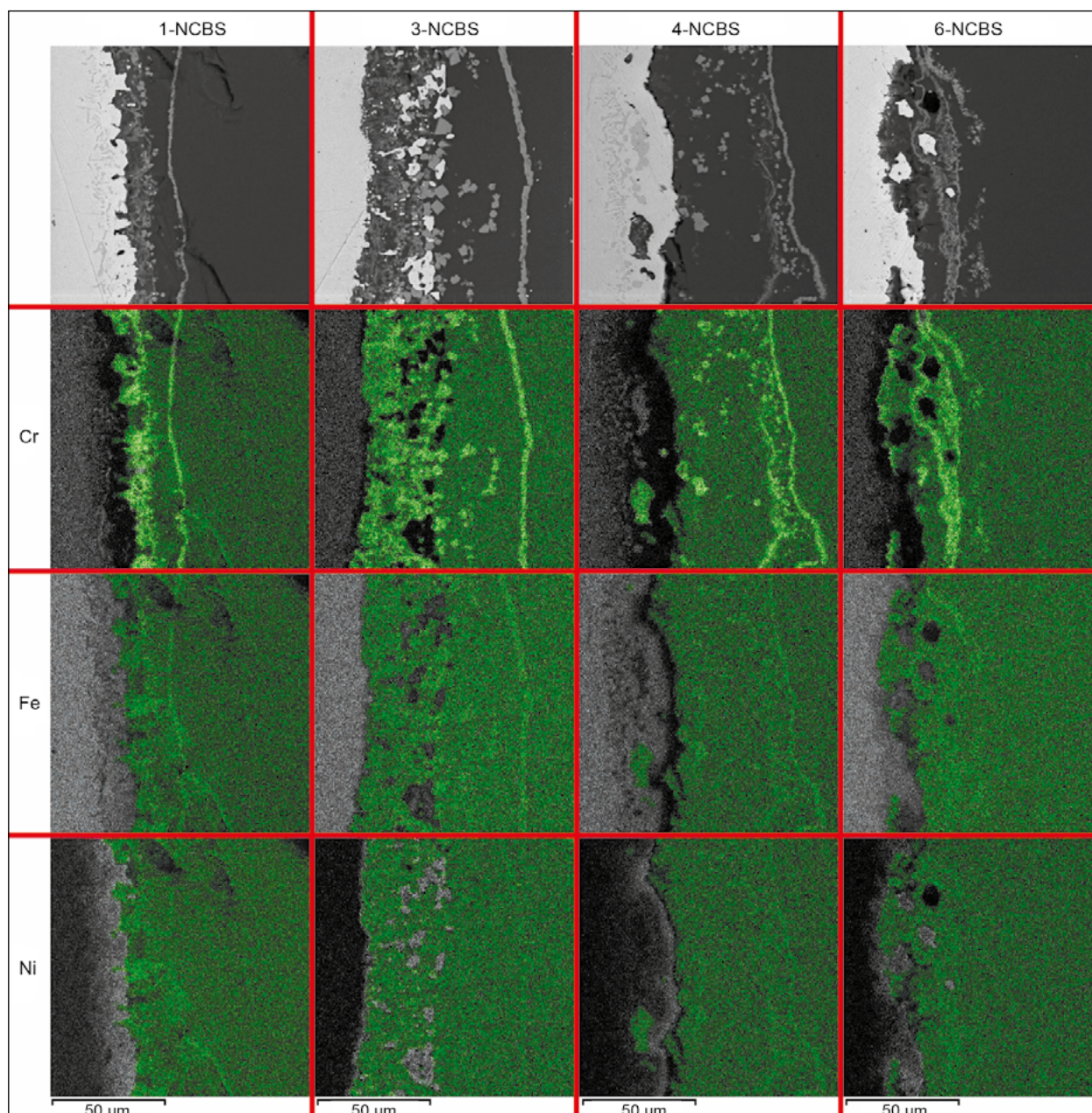


Figure 5. Contact zone between the waste form glass and the container upon completing the electroless nickel plating process (oxygen is indicated in green)

according to its width with the one evaluated under a previous study [10] focused on the interaction of steel grade 08Kh18N10 (AISI 304H) with similar waste form melts: the width turned out to be less, as well as the content of iron and chromium oxides in the solidified waste form material.

The stretched protective film layer of a mixed composition resulting from electroless nickel plating produces a somewhat negative effect, namely, it results in a thicker corrosion zone at the container interface with the waste form melt, which is explained by looser structure of the protective layer and additional soluble compounds being formed.

Differences in the chemical composition of waste form materials, primarily in sodium and calcium

content, affect the difference in the melt viscosities, altering depth of the corrosion zone and their saturation with steel components.

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#### References

1. Stefanovsky S. V., Skvortsov M. V., Stefanovsky O. I., Nikonov B. S., Presniakov I. A., Glazkova I. S., Ptashkin A. G. Preparation and Characterization of

- Borosilicate Glass Waste Form for Immobilization of HLW from WWER Spent Nuclear Fuel Reprocessing. *MRS Adv.*, 2017, vol. 2, no. 11, pp. 583–589. DOI: 10.1557/adv.2016.622.
2. King F. Container Materials for the Storage and Disposal of Nuclear Waste. *Corros.*, 2013, vol. 69, no. 10, pp. 986–1011. DOI: 10.5006/0894.
  3. McCright R. D. Metal Container Materials for Nuclear Waste. *MRS Bull.*, 1994, vol. 19, pp. 39–42. DOI: 10.1557/S0883769400048685.
  4. Shoesmith D. W. Assessing the Corrosion Performance of High-Level Nuclear Waste Containers. *Corros.*, 2006, vol. 62, no. 8, pp. 703–722. DOI: 10.5006/1.3278296.
  5. Guo X., Gin S., Lei P. et al. Self-Accelerated Corrosion of Nuclear Waste Forms at Material Interfaces. *Nat. Mater.*, 2020, vol. 19, no. 3, pp. 310–316. DOI: 10.1038/s41563-019-0579-x.
  6. Guo X., Gin S., Liu H. et al. Near-Field Corrosion Interactions between Glass and Corrosion Resistant Alloys. *npj Mater Degrad.*, 2020, vol. 4, pp. 1–10. DOI: 10.1038/s41529-020-0114-1.
  7. Di Martino J., Rapin C., Berthod P., Podor R., Steinmetz P. Corrosion of Metals and Alloys in Molten Glasses. Part 1: Glass Electrochemical Properties and Pure Metal (Fe, Co, Ni, Cr) Behaviours. *Corros. Sci.*, 2004, vol. 46, no. 8, pp. 1849–1864. DOI: 10.1016/j.corsci.2003.10.024.
  8. Di Martino J., Rapin C., Berthod P., Podor R., Steinmetz P. Corrosion of metals and alloys in molten glasses. Part 2: Nickel and cobalt high chromium superalloys behaviour and protection. *Corros. Sci.*, 2004, vol. 46, no. 8, pp. 1865–1881. DOI: 10.1016/j.corsci.2003.10.025.
  9. Eremyashev V. E., Zherebtsov D. A., Zhivulin V. E., Korinevskaya G. G., Lebedev A. S. Vysokotemperaturnoye vzaimodeystviye khromonikelevoy stali 08KH18N10T i model'nykh matrichnykh borosilikatnykh materialov [High-Temperature Interaction of 08Cr18Ni10Ti Chromium–Nickel Steel with Model Borosilicate Waste Form Materials]. *Neorganicheskiye materialy – Inorganic materials*, 2021, vol. 57, no. 9, pp. 980–986. DOI: 10.1134/S0020168521090041.
  10. Eremyashev V. E., Korinevskaya G. G., Lebedev A. S., Blinov I. A. Vysokotemperaturnoye vzaimodeystviye khromonikelevoy stali s mnogokomponentnymi matrichnymi borosilikatnymi materialami [High-Temperature Interaction of Chromium–Nickel Steel with Multicomponent Matrix Borosilicate Materials]. *Elektrometallurgiya – Russian Metallurgy (Metally)*, 2023, no. 3, pp. 28–37. DOI: 10.31044/1684-5781-2023-0-3-28-37.
  11. Donald I. W. *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*. N. Y.: Wiley, 2010. 507 p.
  12. McCloy J. S., Goel A. Glass-Ceramics for Nuclear-Waste Immobilization. *MRS Bull.*, 2017, vol. 42, no. 3, pp. 233–240. DOI: 10.1557/mrs.2017.8.
  13. Eremyashev V., Osipova L., Shenderovich I. The effects of alkaline earth metals on the structure of sodium borosilicate glasses:  $^{11}\text{B}$  and  $^{29}\text{Si}$  NMR study. *Materials Science Forum.*, 2020, vol. 989, pp. 192–198. DOI: 10.4028/www.scientific.net/MSF.989.192.
  14. Eremyashev V. E., Zherebtsov D. A., Osipova L. M., Danilina E. I. Thermal Study of Melting, Transition and Crystallization of Rubidium and Caesium Borosilicate Glasses. *Ceram. Int.*, 2016, vol. 42, pp. 18368–18372. DOI: 10.1016/j.ceramint.2016.08.169.
  15. Eremyashev V. E., Zherebtsov D. A., Brazhnikov M. P., Zainullina R. T., Danilina E. I. Cerium Influence on the Thermal Properties and Structure of High-alkaline Borosilicate Glasses. *J. Therm. Anal. Calorim.*, 2020, vol. 139, no. 2, pp. 991–997. DOI: 10.1007/s10973-019-08472-6.
  16. Eremyashev V. E., Mironov A. B. Vliyaniye zheleza na strukturu kaliyevykh borosilikatnykh stekol [Effect of Fe on the structure of potassium borosilicate glasses]. *Neorgan. Materialy – Inorganic materials*, 2015, vol. 51, no. 2, pp. 177–181. DOI: 10.1134/S0020168515020065.
  17. Eremyashev V. E., Korinevskaya G. G., Bukalov S. S. Titan v strukture shchelochnykh borosilikatnykh stekol [Titanium in the Structure of Alkali Borosilicate Glasses]. *Steklo i keramika – Glass Ceram*, 2016, vol. 72, pp. 405–408. DOI: 10.1007/s10717-016-9798-7.
  18. Fluegel A. Glass viscosity calculation based on a global statistical modelling approach. *European Journal of Glass Science and Technology. Part A: Glass Technology*, 2007, vol. 48, no. 1, pp. 13–30.

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## Processing, Conditioning and Transportation of Radioactive Waste

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