Corrosion Behavior of NiCu Low-Alloy Steel in Deoxygenated NaHCO3 Solution Containing Cl-: Postprint

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Abstract

NiCu low-alloy steel is a highly promising candidate material for high-level waste geological disposal containers. This work conducted in-situ monitoring of the evolution of open-circuit potential curves and impedance spectra for NiCu low-alloy steel under long-term immersion in a simulated deep groundwater environment (a deoxygenated 0.1 mol/L NaHCO3 + 0.1 mol/L NaCl solution) to investigate corrosion evolution on the electrode surface, with comparison to low-carbon steel under identical conditions. The results demonstrate that the corrosion resistance of NiCu low-alloy steel in the test solution is significantly superior to that of low-carbon steel, particularly its localized corrosion resistance. The alloying element Ni enriches in the inner rust layer, possibly in the form of NiFe2O4, whereas Cu enrichment is not pronounced, with CuFeO2 considered as a possible existing form.

Full Text

Preamble

The Corrosion Behaviour of NiCu Low Alloy Steel in a Deaerated Bicarbonate Solution Containing Cl Ions

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Abstract

NiCu low alloy steel is a promising candidate canister material for the geological disposal of high-level radioactive waste (HLW). Due to the intensely radioactive nature of HLW, the waste must be isolated from the biosphere for many tens of thousands of years. Deep geological disposal is now considered the most preferable option for isolating HLW and relies on a series of natural and engineered barriers, including a metallic canister. However, once the waste package is emplaced, groundwater will slowly seep back through the outer barriers and ultimately reach the canister surface, leading to groundwater-induced dissolution of the canister and subsequent transport of radionuclides through the barriers. Thus, the effectiveness of radionuclide retention and isolation depends primarily on the corrosion resistance of metallic canisters in deep groundwater environments.

This study investigated the corrosion evolution of NiCu low alloy steel under long-term immersion conditions in a simulated deep groundwater environment (deaerated 0.1 mol/L NaHCO + 0.1 mol/L NaCl solution) through in-situ monitoring of open-circuit potential variations and impedance spectroscopy evolution. The results were compared with the corrosion behavior of low carbon steel under identical conditions. The electrochemical results demonstrate that NiCu low alloy steel exhibits significantly superior corrosion resistance compared to low carbon steel, particularly in terms of resistance to localized corrosion. The alloying element Ni was found to be enriched in the inner rust layer, likely existing as NiFe O , while Cu enrichment was less pronounced and may exist as CuFeO .

Keywords: low alloy steel; rust layer; HCO ; Cl

Introduction

The international community currently favors deep geological disposal for high-level radioactive waste, and China intends to adopt this approach as well [?]. In this scheme, the metal canister serves as the first engineered barrier for storing vitrified HLW, making its service life a critical factor for successful waste disposal. During long-term geological disposal, groundwater will gradually diffuse to the canister surface, corroding the metal and eventually causing failure. Various metallic materials including carbon steel, copper, titanium alloys, and nickel-based alloys have been evaluated for different geological disposal environments worldwide [?]. Among these, carbon steel is considered quasi-corrosion-resistant with a finite corrosion rate but low susceptibility to localized corrosion, allowing for service life predictions under disposal conditions.

However, studies [?, ?] have revealed that in groundwater environments, carbon steel exists in a reactivated state after passivation with a relatively high corrosion rate. When the solution contains SO ^{2} , the metal surface exhibits uniform corrosion morphology, whereas Cl induces localized corrosion morphology. This indicates that in actual disposal scenarios, carbon steel canisters would have high corrosion rates due to reactivation, and the presence of aggressive ions in groundwater could lead to localized corrosion pitting or stress corrosion cracking, failing to meet the design requirements for container longevity. Therefore, from both economic and safety perspectives, it is necessary to investigate alloy modification to improve the corrosion resistance of carbon steel by adding alloying elements that enhance performance in groundwater environments.

Nishimura et al. [**?**] studied the atmospheric corrosion resistance of low alloy steels containing Co or Ni, finding that Co likely exists as trivalent ions in FeOOH, helping the rust layer block aggressive anions like Cl , though this effect was only significant in early stages. Ni likely exists as divalent ions in Fe O , increasing the density of the inner rust layer with more pronounced effects in later stages. Wang et al. [**?**] obtained corrosion rate curves for weathering steel and carbon steel containing Cr, Cu, P, and Ni in three atmospheric environments over five years, attributing the low corrosion rate of weathering steel to alloying element enrichment in the rust layer. Cao et al. [**?**] compared the pitting corrosion resistance of Ni-Cu-P steel, Cu-containing low alloy steel, and carbon steel in seawater splash zones, demonstrating that Ni-Cu-P steel exhibited superior uniform and pitting corrosion resistance compared to carbon steel. In fact, Ni-Cu-P series low alloy steel has been commercially produced in the United States since 1964 as a steel grade with excellent corrosion resistance in seawater splash zones [**?**]. Additionally, NiCu low alloy steel has seen significant development in Japan in recent years, primarily for use in high-Cl environments such as marine atmospheres [**?**]. However, no reports have been published on the applicability of such steels to HLW geological disposal environments.

Therefore, this work selected NiCu low alloy steel as a candidate canister material for HLW geological disposal and investigated its corrosion behavior in deaerated NaHCO solution containing Cl , comparing it with the corrosion behavior of carbon steel under identical conditions.

Experimental Methods

A three-electrode system was employed with an electrolyte solution of 0.1 mol/L NaHCO + 0.1 mol/L NaCl. The test specimens were bulk samples of NiCu low alloy steel and Q235 low carbon steel, with chemical compositions shown in . Both had dimensions of 10 mm × 10 mm × 3 mm. The working electrode area was 100 mm^2, with remaining surfaces sealed with epoxy resin. The reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was a Pt sheet. For long-term immersion tests of NiCu low alloy steel, in addition to one working electrode sample, three additional bulk samples were prepared in the same container for subsequent analysis. All samples were ground sequentially with sandpaper to 800 grit, rinsed with deionized water, degreased with ethanol, and dried before use.

Prior to experiments, high-purity N (99.999%) was continuously purged through the sealed electrolytic cell to deaerate the solution. Simultaneously, specimens were lightly polished on 800-grit sandpaper with the same electrolyte solution to remove surface films before immediate immersion. After 30 minutes of continued N purging, measurements commenced, with a water-sealed bottle maintaining N atmosphere in the cell headspace throughout the experiment. Polarization curves were measured using a PARSTAT 2273 electrochemical workstation. After the open-circuit potential stabilized, specimens were polarized from -1.0 V to 0.4 V at a scan rate of 10 mV/min. Long-term in-situ corrosion potential monitoring was performed using an HA-151A potentiostat, pausing only for impedance measurements. All potentials were reported relative to SCE. Electrochemical impedance spectroscopy was measured using the PARSTAT 2273 workstation over a frequency range of 0.01 Hz to 100 kHz.

After the immersion test, the three bulk samples from the sealed cell were removed, dried under high-purity N flow, and stored sealed. A Shimadzu XD-5A X-ray diffractometer (XRD) analyzed corrosion products on one specimen (No. 1). The corrosion products were then removed using pickling solution (20 g (CH) N + 500 mL HCl + 500 mL H O), and surface morphology was examined using an FEI XL-30FEG scanning electron microscope (SEM). A second specimen (No. 2) was encapsulated in epoxy, slowly ground to a polished cross-section with 400-grit sandpaper, rinsed with deionized water, degreased with ethanol, and dried. Cross-sectional corrosion morphology was observed via SEM, with energy-dispersive spectroscopy (EDS) performing line scans across the rust layer. A Shimadzu EPMA-1610 electron probe microanalyzer (EPMA) further conducted elemental mapping of the cross-section. The final specimen (No. 3) had its loose outer rust layer removed with stainless steel foil, and the inner rust layer was analyzed for alloying element valence states using a Thermo ESCALAB250 X-ray photoelectron spectroscopy (XPS) system.

2.1 Comparison of Corrosion Resistance Between NiCu Low Alloy Steel and Carbon Steel

The dashed line in [Figure 1: see original paper]a shows the polarization curve of NiCu low alloy steel in deaerated NaHCO solution containing Cl . The corrosion potential was approximately -0.780 V, with hydrogen evolution dominating the cathodic reaction. The anodic behavior can be described as comprising activation, passivation, stable passivation, and reactivation regions. In the activation region (-0.78 to -0.63 V), anodic corrosion current density increased rapidly with positive potential shift. In the passivation region (-0.63 to -0.48 V), current density decreased significantly with potential, indicating formation of a protective product film with gradually increasing protective capability. In the stable passivation region (-0.48 to -0.20 V), current density fluctuated around

2.7 A/cm^2 (maximum 4.5 A/cm^2, minimum 1.25 A/cm^2) rather than showing monotonic behavior, likely due to competitive adsorption between aggressive Cl and protective HCO . Beyond -0.20 V, the specimen entered the reactivation region, where anodic current density increased exponentially to the anodic limiting diffusion current density.

Under identical conditions, the polarization curve for carbon steel is shown as the dashed line in [Figure 1: see original paper]b [?]. Compared with NiCu low alloy steel, carbon steel exhibited a more negative corrosion potential at approximately -0.810 V, with both materials showing hydrogen evolution-dominated cathodic regions. However, in the anodic region, carbon steel' s passivation potential was more negative at approximately -0.658 V, and unlike NiCu steel, it rapidly entered reactivation (pitting) after the passivation region without a stable passivation interval. Furthermore, the minimum anodic current density before reactivation was 13.44 A/cm^2 for carbon steel—nearly an order of magnitude higher than NiCu steel' s stable passivation current density. These results demonstrate that NiCu low alloy steel possesses superior corrosion resistance in the test solution, with passivation films forming more readily and remaining more stable, and its corrosion rate before reactivation being approximately one order of magnitude lower than that of carbon steel.

The solid line in [Figure 1: see original paper]a shows the open-circuit potential (OCP) evolution of NiCu low alloy steel during 28 days of immersion in deaerated NaHCO solution containing Cl . The curve can be divided into three stages: a low-potential region before transition, a high-potential transition region, and a stable high-potential region. During the first 3 days, OCP remained stable at approximately -0.77 V, close to the corrosion potential from polarization curves, indicating no protective corrosion product film covered the surface initially. After day 3, OCP began slowly shifting positive with fluctuations, suggesting gradual formation of protective corrosion products. By day 11, OCP had risen to approximately -0.70 V, then abruptly jumped to approximately -0.50 V within half a day, indicating a fundamental change in the surface corrosion products. Comparison with polarization curves suggests the electrode surface likely entered the passivation region, where the corrosion product film became relatively protective. In the second stage (days 11-20), OCP exhibited oscillations after the initial rise, with maximum values of -0.45 V (stable passivation region) and minimum values of -0.58 V (passivation region), indicating simultaneous rupture and repair of the protective film. In the third stage (after day 20), OCP stabilized at approximately -0.52 V, suggesting the NiCu low alloy steel surface reached a stable condition near the Flade potential after 28 days, approaching a passive state.

The OCP evolution of carbon steel during 35 days of immersion is shown as the solid line in [Figure 1: see original paper]b [?]. Carbon steel exhibited a simpler two-stage behavior. In the first stage (first 20 days), OCP slowly increased from -0.81 V to approximately -0.76 V. After a rapid transition, the second stage began. In this stage (after day 20), OCP shifted positive to a maximum of approximately -0.48 V, corresponding to the reactivation (pitting) region where the protective corrosion product film began losing its effectiveness. Subsequently, OCP shifted slightly negative to approximately -0.52 V, corresponding to the boundary between passivation and pitting, indicating unstable surface films. Thereafter, OCP showed a slow upward trend toward reactivation, with occasional drops to approximately -0.56 V, suggesting transitions toward passivation. These fluctuations demonstrate the instability of carbon steel’ s corrosion products. In summary, NiCu low alloy steel’ s OCP ultimately stabilized in the later passivation region with better protective films and lower corrosion rates, while carbon steel’ s OCP stabilized in the post-passivation reactivation (pitting) region with deteriorating protective films and higher corrosion rates.

Electrochemical impedance spectra measured at different immersion times for both materials are shown in [Figure 2: see original paper]. During the first stage (first 11 days), NiCu low alloy steel’ s Bode phase plots exhibited a single phase angle peak that shifted toward lower frequencies with immersion time, decreasing from approximately 6 Hz to 1 Hz, while the peak magnitude increased slightly from 65° to 70°. Diffusion characteristics appeared in the low-frequency region but weakened with time. Correspondingly, Bode impedance plots showed decreasing impedance: low-frequency (10 mHz) impedance decreased from 3250 $\Omega \cdot \mathrm{cm}^2$ to approximately 1783 $\Omega \cdot \mathrm{cm}^2$, and high-frequency (10 kHz) impedance decreased from 17.4 $\Omega \cdot \mathrm{cm}^2$ to approximately 10.1 $\Omega \cdot \mathrm{cm}^2$. Thus, during the first stage, corrosion became easier with increasing immersion time, indicating that the formed corrosion products were not protective and may have accelerated substrate corrosion through galvanic effects.

After the potential transition (after day 11), the Bode phase plots changed significantly, no longer showing a single symmetric peak. This phenomenon typically indicates superposition of multiple time constants. In the high-frequency region (100 Hz to 10 kHz), a weak phase angle peak appeared, while in the low- and mid-frequency regions (<100 Hz), an extremely asymmetric broad peak resulted from the superposition of at least two time constants. Since the test solution was a mixed NaHCO and NaCl solution, different corrosion modes (uniform corrosion, pitting, etc.) could occur in different regions when HCO and Cl accumulated separately, leading to multiple time constants [?]. After the potential transition, impedance curves showed some overlap, particularly in the high-frequency region (>100 Hz). Low-frequency impedance increased slightly with immersion time, likely due to formation of a more protective corrosion product film in the later third stage.

Carbon steel’ s EIS results ([Figure 2: see original paper]c) also showed a single phase angle peak in the first stage (first 20 days), which shifted slightly toward lower frequencies from approximately 4.6 Hz to 2.4 Hz, with peak magnitudes remaining around 63°. Weak diffusion characteristics in the low-frequency region diminished with time. Some high-frequency phase shift was detected but considered experimental error [?, ?]. The three measured curves in the first stage essentially overlapped. After the potential transition (after day 20), both phase angle and impedance curves changed markedly, showing multiple time constant superposition similar to NiCu steel. A weak peak appeared in the high-frequency region (>10 Hz) that increased with immersion time, while a broad asymmetric peak in the mid-to-low frequency region (<10 Hz) indicated at least two time constants, with peak magnitude decreasing over time. Impedance increased with immersion time except at the lowest frequencies.

Two corresponding equivalent circuits were selected for fitting the impedance spectra, as shown in [Figure 3: see original paper]. [Figure 3: see original paper]a fits the EIS data obtained before the OCP transition (Stage I), where R represents solution resistance, Q double-layer capacitance, R charge transfer resistance, W Warburg impedance, and Q high-frequency capacitance (present only in carbon steel data, shown with dashed connection). [Figure 3: see original paper]b fits the EIS data after the OCP transition (Stages II and III), where Q and R represent capacitance and resistance of the precipitated corrosion product layer, Q and R those of pitted areas, and Q and R those of passive areas [?]. Q is also shown with dashed connection as it appeared in later carbon steel data but never in NiCu steel data.

Fitting results are listed in and . The constant phase element (CPE) impedance Z depends on angular frequency : Z = Y ^{1}(j) . Each CPE has two parameters: Y (units S·s ·cm ^{2}) and dimensionless exponent n (-1 n 1). Depending on n, CPE can represent inductance (n = -1), resistance (n = 0), Warburg impedance (n = 0.5), or pure capacitance (n = 1).

shows that both R and R for NiCu steel decreased with immersion time, indicating easier corrosion progression, while Y , increased. The n values remained above 0.8, likely due to corrosion product deposition. These newly deposited products were mostly non-protective and loosely structured, increasing interfacial capacitance [?]. Carbon steel showed no clear trends for R , R , or Y , , indicating stable corrosion during Stage I. Both materials exhibited uniform corrosion in this stage.

After the potential transition, both materials' corrosion behavior changed significantly. As shown in [Figure 3: see original paper] and , a corrosion product layer precipitated on the external surface, represented by Q and R . NiCu steel showed larger Y , and smaller R , while carbon steel showed larger R and smaller Y , with n near 0.8. This suggests NiCu steel' s outer product layer was more porous and non-protective than carbon steel' s. At the corrosion product/substrate interface, both materials transitioned from uniform corrosion to a composite state of two corrosion behaviors (pitting and passivation). NiCu steel' s R , Y , , and n remained relatively stable, while carbon steel showed significant variations—Y , and R were large after 24 days but decreased substantially after 32 days, possibly indicating pitting behavior. In passive regions, NiCu steel' s Y , remained stable with n near 0.5, indicating diffusion-blocking capability, while R increased from Stage II to III, suggesting reduced corrosion rates. Carbon steel' s Y , remained low but increased with time, while R decreased, indicating increased corrosion rates in passive regions during later immersion stages.

Previous work [?] demonstrated obvious corrosion pits on carbon steel after 30 days of immersion. [Figure 4: see original paper] shows the surface morphology of NiCu low alloy steel after rust removal. At the same magnification as the carbon steel image in [?], NiCu steel exhibited uniform corrosion morphology ([Figure 4: see original paper]a), while carbon steel showed localized corrosion. At 5000× magnification ([Figure 4: see original paper]b), fine voids were observed, identified as metastable pitting pits predominantly located at weak grain boundary regions. Thus, under identical conditions, carbon steel underwent pitting after immersion, while NiCu low alloy steel primarily exhibited uniform corrosion with only fine metastable pits observed at high magnification. This indicates that Ni and Cu alloying elements inhibit localized corrosion and promote uniform corrosion.

2.2 Mechanism of Alloying Elements

[Figure 5: see original paper] shows the XRD pattern of NiCu low alloy steel after 28 days of immersion. The corrosion products consisted mainly of -FeOOH, Fe O , and Fe (OH) CO , with no detectable Ni or Cu phases.

To further investigate whether Ni and Cu existed in the corrosion products, EDS and EPMA analyses were performed on cross-sections of the rust layer, as shown in [Figure 6: see original paper]. [Figure 6: see original paper]a presents the SEM cross-sectional morphology, with the lightest region being the metal substrate, the darkest being epoxy resin, and the intermediate region being the corrosion product film. The rust layer divided into a loose, poorly protective outer rust layer and a dense inner rust layer. [Figure 6: see original paper]b and c show line scan results for Ni and Cu, respectively. Ni content in the inner rust layer exceeded that in the substrate, showing clear enrichment that decreased significantly with distance from the substrate in the outer layer. Cu content in the inner rust layer was similar to that in the substrate, decreasing slightly with distance in the outer layer. [Figure 6: see original paper]d is an enlarged view of [Figure 6: see original paper]a, with [Figure 6: see original paper]e and f showing EPMA mapping results for Ni and Cu, respectively. EPMA results confirmed Ni enrichment in the inner rust layer, while Cu content in the substrate and inner rust layer was higher than in the outer layer, though no obvious Cu enrichment was detected in the inner rust layer. Due to the relatively low Cu content in this low alloy steel, EDS and EPMA could not easily resolve distribution differences between the rust layer and substrate. Literature [?, ?] indicates that alloying element enrichment in the inner rust layer helps form a dense inner layer, thereby improving corrosion resistance.

[Figure 7: see original paper] shows XPS analysis of Ni and Cu in the inner rust layer after 28 days of immersion. The Ni 2p / peak at 855.8 ± 0.1 eV was close to the NiO database value, though XRD detected no NiO, suggesting Ni likely exists as divalent ions in Fe oxides, possibly as NiFe O . NiFe O forms when Ni substitutes for Fe in the Fe O crystal lattice, which is difficult to distinguish due to similar atomic radii. However, NiFe O possesses higher thermodynamic and electrochemical stability than Fe O and has a negative charge structure that effectively blocks aggressive anions, reducing substrate corrosion [?]. Thus, NiFe O presence in the inner rust layer benefits corrosion resistance in Cl - containing solutions. The Cu 2p / peak at 932.7 ± 0.1 eV indicated Cu likely exists as monovalent Cu(I), possibly as CuFeO , though the low Cu content prevented XRD detection.

[Figure 8: see original paper] shows the E-pH diagram for the Fe-Ni-Cu-H O system at 25°C. Under long-term immersion, the NaHCO buffer solution maintained pH around 8.33. Within the studied potential range, the most probable Ni and Cu species are NiFe O and CuFeO [?, ?]. As shown in [Figure 8: see original paper], the stability regions of NiFe O , CuFeO , and Fe O overlap in the E-pH diagram, indicating these three Fe oxides can coexist stably under certain conditions. Based on solution pH and OCP fluctuations in Stages II and III, the electrode potential and solution pH varied within the shaded region in [Figure 8: see original paper], which lies within the overlapping thermodynamic stability region of these three species. This supports the conclusion that NiFe O , CuFeO , and Fe O likely coexist in the rust layer, particularly in the inner layer, providing protective effects.

Conclusions

1) Compared with carbon steel, NiCu low alloy steel ultimately stabilizes in the later passivation region rather than the pitting activation region after long-term immersion, exhibiting lower corrosion rates and uniform rather than localized corrosion morphology.
2) The alloying elements Ni and Cu exist in the inner rust layer as NiFe O and CuFeO , respectively, thereby improving the corrosion resistance of the metallic material.

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Note: Figure translations are in progress. See original paper for figures.