Josephinite

Description: Alloy 22 has been selected as the container material in the proposed concept for high-level nuclear waste disposal at Yucca Mountain, Nevada. The material is nickel-based metal (Ni 56%), alloyed with 22% of chromium, other main components being: Mo 13%, W 3%, Fe 3%, Co 2.5% (Hastelloy C-22™, Haynes International Inc). A characteristic to the metal alloy is its high corrosion resistance in oxidizing conditions. The corrosion resistance is largely attributed to the formation of oxide (mainly chromium oxide) layer on the canister surface. The waste package system consists of the corrosion-resistant canister which sits on an emplacement pallet that is made of plates of Alloy-22. The supporting inner structural shell and lid of the canister are to be manufactured from stainless steel (type 316NG), providing structural integrity (Bechtel SAIC Co. 2002). The corrosion resistance and strength of this iron-based material is largely attributed to the alloying chromium (about 16%), nickel (about 12%) and molybdenum (about 3%).

These metal alloys being considered for use in the nuclear waste packages have been developed during the last decades (stainless steels from the early decades of the 20^{th} century onwards). Consequently, the experience on their corrosion resistance is mainly derived from the testing and development of the materials. However, the long-term behaviour of metals with similar basic characteristics can be observed in certain natural occurring phases. The relative stability of nickel-rich iron alloys over iron-rich ones has been observed in meteorites, although the time frame and exposure history of the occurrences is often poorly known. Terrestrial nickel-iron is rare on the earth's surface, but has been observed in small amounts in ultramafic rocks.

The occurrence of nickel-iron metal in josephinite, a rare rock type found in Oregon, has been studied as a natural analogue of the long-term behaviour of nickel-based metallic materials. Corrosion resistance of nickel-based alloys as well as that of stainless steel is mainly attributed to the formation of microscopic chromium oxide layer on the surface. Naturally occurring chromium oxide, chromite ($FeCr_2O_4$) is often associated with mafic and ultramafic rocks. The occurrence of chromite associated with chromium-bearing groundwaters at Sierra de Guanajuato has been studied as a natural analogue of the behaviour of the passive surface layer of steel and nickel-alloys. Josephinite is a rock type containing nickel-iron minerals awaruite Ni_3Fe (also known as mineral josephinite) and taenite (γ-Ni,Fe). Josephinite of the type locality Josephine County, SW Oregon, is associated with the ultramafic Josephine Peridotite, part of the Josephine Ophiolite Complex. The ophiolite complex represents ocean crust and upper mantle formed 165 million years ago and formed along the western margin of North America by seafloor spreading in a deep water-basin situated above a subduction zone, where the ancient Pacific plate was thrust beneath western North America.

Josephinite samples from the ophiolite complex are mainly found as pebbles in stream placers of Josephine creek and the near-by Mendenhall creek near the town Cave Junction (Figure 1). Nickel-iron nuggets found are mostly rounded and their size is in the range of 1 to 10 cm. The age of the terrace gravel of the creeks has been estimated to be of the order of 1 million years. Laterite soil deposits above the Josephine creek are about 6 million years old, suggesting that the peridotite, source of the detrital josephinite, has been exposed to chemical weathering at least that time.

The origin of terrestrial nickel-iron was earlier ascribed to the serpentinization of ultramafic plutonite (harzburgite). Dick (1974) pointed out that the josephinite occurrences are associated with strongly serpentinized shear zones in harzburgite. Josephine creek valley represents one of the major shear zones. The theory implies that formation of nickel-iron alloy was a result of low-temperature metamorphism of ultra-basic rocks. More specifically, reduction of iron and nickel of sulphides and silicates by hydrogen formed in serpentinization process. Small amounts of metallic iron, formed in that type of process is found in many serpentinites.

Bird et al. (1974) proposed that josephinite of Oregon originated in the core-mantle region (at depths of more than 2000 km), and was transported to the upper lithosphere by a deep-mantle plume and was then emplaced onto the upper crust with the obduction of the ophiolite sequence.

Isotopic information suggests that josephinite may have crystallized as much as 1.4 billion years ago (Bird et al., 1999).

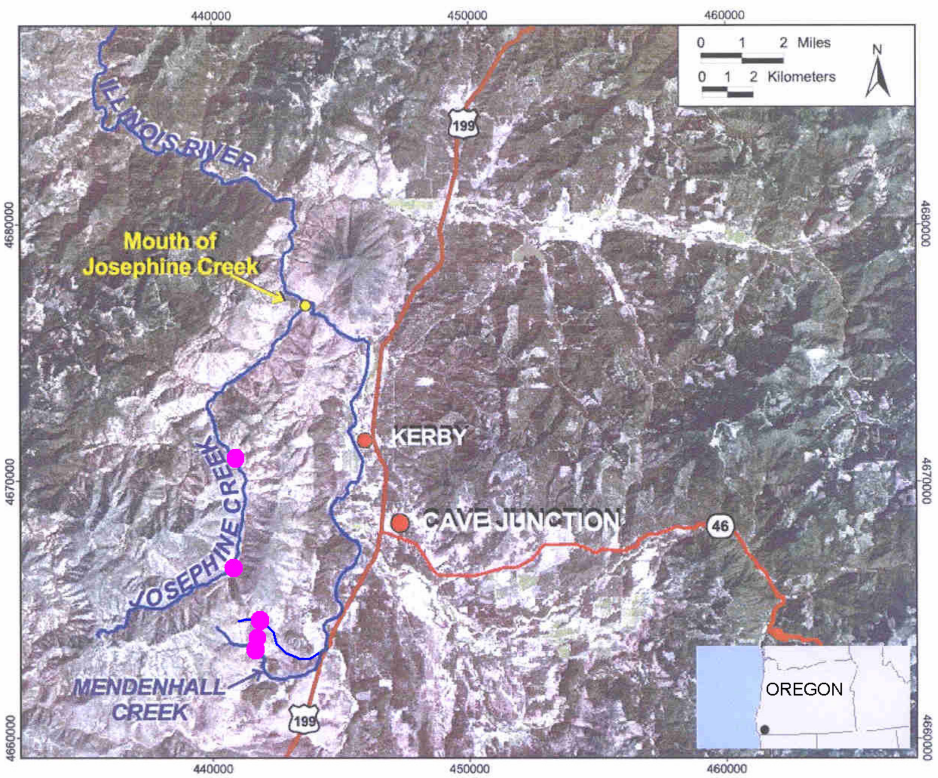

Figure 1. Satellite image of the Josephine Cave Junction area, Josephine County, S-W Oregon, U.S.A (Cragnolino et al. 2004). Occurrences of josephinite-bearing placers (•) are based on Dick 1974).

The corrosion behaviour of natural josephinite has been studied in many sets of electrochemical experiments and compared with the behaviour of cast Ni_3Fe alloy. The experiments indicated that the corrosion of both materials is inhibited by passivation due to the formation of oxide/hydroxide film on the metal surface.

Josephinite and awaruite are very stable rock and mineral phases, as demonstrated by their survival for millions of years with only minor amounts of oxidation. The josephinite nuggets have alteration rims comprised of outer iron-dominated oxide (Fe_3O_4) and inner $NiFe_2O_4$ (trevorite). Some samples of josephinite contain the high-temperature phase taenite (a disordered Ni-Fe metal) in addition to awaruite. Phase relation studies of the Fe-Ni system suggest that taenite is not stable below ~350℃ so the persistence of taenite for millions of years suggests that low-temperature phase change rates for taenite are exceedingly slow. X-ray photoelectron spectroscopic analysis of a josephinite placer sample from the Josephine Ophiolite revealed that while both iron and nickel are oxidized on the surface, nickel remains in reduced (metallic) form at depths of 2 nm and greater. Due to its high nickel concentrations, the longevity of josephinite indicates that nickel alloys will have long-term phase stability.

Whilst josephinite does not contain the molybdenum and tungsten that serve as stabilizing elements in Alloy 22 passivation films, its ability to resist corrosion provides confidence that Alloy 22 will remain passive under repository conditions.

In addition to nickel, chromium is a key component of the corrosion resistant metallic materials like Alloy 22 and stainless steels. Chromite ($FeCr_2O_4$) is the main mineral of commercial value in chromium ores, being often associated with mafic and ultramafic intrusions. Chromite is very resistant against both chemical weathering and mechanical denudation, as indicated by its common presence in placer deposits.

Chromium-bearing ultramafic rocks were studied as a potential source of the relatively high chromium concentration in groundwaters of León Guanajuato Valley, Central Mexico (Robles-Camacho & Armienta 2000). Weathering of ultramafic rocks of Sierra de Guanajuato (chromium contents around 1500 ppm) produced contamination levels in the range of 0.004 to 0.015 mg/l of Cr(VI), mainly to the northeast of the valley (Armienta-Hernández and Rodríguez-Castillo 1995). However, the main sources of chromium contamination of the area are anthropogenic (leather tanning, metal plating and chromium-bearing fertilizers).

The ultramafic rocks of Sierra de Guanajuato are Jurassic (about 150 million years old) serpentinized pyroxenite. Serpentinization has led to partial mobilization of chromium and other ions, and exsolution of secondary phases. The release of chromium from serpentines and pyroxenites has been studied in the laboratory under strongly acid oxidizing conditions (mixture of HCl and HNO_3) where the disintegration of exsolution borders appeared to be the main geochemical process of chromium release from chromite to water, while chromite itself shows notable resistance against corrosion.

Relevance: These analogues demonstrate the long-term stability of nickel- and iron-based alloys, when passive layer on the surface remains stable.

Position(s) in the matrix tables: Near-field, Mechanical integrity of barriers, corrosion

Limitations: Josephinite does not contain chromium, which is the main alloying element conferring passivity of Alloy 22. A major source of chromium in groundwaters of Sierra de Guanajuato is the anthropogenic contamination.

Quantitative information: Electrochemical (anodic) behaviour of natural metallic material vs. manufactured metal.

Uncertainties: The evolution of the environment of josephinite occurrences cannot be assessed reliably.

Time-scale: From hundreds of thousand to millions of years.

PA/safety case applications: None known.

Communication applications: None known.

References:

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Added value comments: None to add.

Potential follow-up work: None known.

Keywords*:* near-field, waste package, alloys, corrosion

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