IMOA®
INTERNATIONAL MOLYBDENUM ASSOCIATION

NEWSLETTER

JANUARY 2003

Membership

Welcome to 3 new members in 2003.

Barex Resources, Inc.
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Produces and recycles heavy metals, primarily tungsten and molybdenum. Its daughter company, Uzmetal Technology Ltd in Uzbekistan, produces about 1000 tons Mo per year, MoO3, Mo Powder and sintered materials.

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Traders of molybdenum products

Email and website addresses

Please note these have been changed to:

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AGM in 2003

Jinduicheng Molybdenum Mining Corporation (the biggest producer in China) has kindly offered to host this event in Shanghai during the week beginning 20 October. The programme is under discussion and details will be announced on IMOA's website and in the July Newsletter.

New IMOA Publications Available

IMOA has recently published four new brochures geared towards the architecture, building and construction (ABC) market. The guide "Which Stainless Steel Should I Specify for Exterior Applications" gives an overview of the material selection process for demanding outdoor applications. Additionally, there are three case studies that illustrate different demanding environments and good and bad material selection.

Hard copies are available from the Secretariat; an electronic copy can be downloaded from IMOA's website. More case studies are planned to be released approximately every three months.

Moly Does the Job

This case study has been provided by Thomas Stoner of Hercules Incorporated and Kelly Wyrough of Roben Manufacturing and was written by IMOA consultant John Grocki. The views and opinions expressed here are those of the authors and not Hercules or any subsidiary of Hercules Inc.

Stainless Steel with 6% Mo Improves Equipment Efficiency and Eliminates Costly Repair.

SUMMARY

A major chemical company producing chemicals for the pulp and paper industry had been using jacketed process reactor vessels made from carbon steel on the water side and clad with 2% molybdenum-containing Type 316L (UNS S31603, EN 1.4404) stainless steel on the process side. These vessels required frequent repairs of the carbon steel cooling/heating jacket and vessel exterior. Corrosion testing and a cost evaluation resulted in the replacement of the clad vessel with a solid 6% molybdenum stainless steel vessel. It is expected to provide years of maintenance-free service.

THE PROCESS

The process vessel (***Figure 1***) is used to heat and cool a process stream. The chemical is heated with plant steam to a temperature of 275°F (135°C) and cooled with cooling tower water to a temperature of 50°F (10°C). The vessel is cycled through this sequence three times per day.

Type 316L stainless steel was chosen for the process side to provide corrosion resistance against the chemical and to maintain product cleanliness. Carbon steel was chosen for the water side to avoid chloride stress corrosion cracking (CSCC) at elevated temperatures and at steam and water chloride levels expected to exceed 150 ppm.

THE CORROSION

General and oxygen cell pitting corrosion occurred on both the carbon steel half pipe cooling jacket and the carbon steel exterior vessel wall. The attack occurred over the entire surface but was slightly more aggressive in weld areas where slag inclusions or lack of penetration was apparent.

Historically, the corrosion caused leaks in the carbon steel half pipe jacket and thinning of the carbon steel side of the stainless clad vessel wall. Frequent repair welding was required to stop the leaks and to build back the lost wall thickness. Eventually the problem became significant enough to downgrade the pressure rating for the vessel. A complete replacement of the vessel was required.

The Type 316L stainless cladding was fully resistant to the process side environment.

THE SOLUTION

Ideally, a construction material should be selected that withstands both CSCC on the steam side and the chemical on the process side. Type 316L stainless steel does provide sufficient resistance to the process environment, but, based on extensive field experience, cannot be expected to resist CSCC on the steam side. ***Figure 2***, which summarizes field experience in Types 304 / 304L (UNS S30400/30403, EN 1.4301/1.4307) and 316/316L (UNS S31600/S31603, EN 1.4401/1.4404) and extrapolates from laboratory tests for higher alloyed grades, shows that Type 316L will suffer from CSCC at the heating temperature of 275°F (135°C) at chloride levels below approximately 10ppm. Even duplex stainless steel such as 2205 (UNS S32205 or S31803,EN 1.4462) which generally provides much better resistance to CSCC than Type 316 is expected to stress crack under the operating conditions. Based on this figure, the group of super austenitic 6% molybdenum stainless steels (e.g. UN S31254, N08926 or N08367; EN 1.4547, 1.4529), should provide sufficient resistance to CSCC under the operating conditions. They should also be at least as resistant to the process environment as the lower-alloyed Type 316L stainless steel and were therefore selected as a candidate material.

Figure 1: *Process vessel constructed in 6% molybdenum stainless steel.*

Corrosion coupons of 6% molybdenum stainless steel were installed in the existing equipment for a one-year period to determine if it was a suitable replacement material. The 6% molybdenum grades showed corrosion rates of less than 2 mpy (0.05 mmpy) and no initiation of CSCC.. One of them was therefore selected as material for the replacement vessels.

THE COST SAVINGS

Use of the higher strength 6% molybdenum stainless steel provided a significant reduction in the required vessel wall thickness. This resulted in cost savings of almost 30% in material and fabrication cost compared to a clad vessel. Additionally, operating advantages were gained since the reduced wall thickness results in better heat transfer. The improved corrosion resistance on the process side, while not initially required, provides flexibility for future process changes. Finally, the jacket side corrosion resistance provides a significant savings in long-term maintenance cost. It is estimated that the repair cost of the carbon steel exceeded $500,000 every five years.

Note: 254 SMO, AL-6XN, Cronifer 1925hMo – alloy 926 and INCOLOY alloy 25-6MO are 6% molybdenum stainless steels. Their names are registered trademarks of AvestaPolarit, ATI Properties, ThyssenKrupp VDM and Special Metals, respectively.

Figure 2: *Limits for chloride stress corrosion cracking in cooling waters as a function of chloride content and water/steam temperature. The 6% Mo stainless steel curve is also valid for super duplex stainless steels such as 2507. (UNS S32750, EN 1.4410) (Adapted from Nickel Development Institute Reference Book Series No 11 021, High Performance Stainless Steels, Figure 63).*

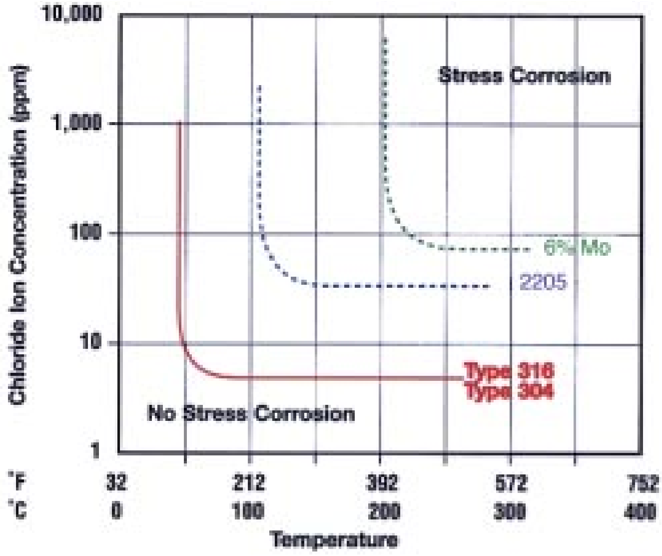

Table 1: *Typical chemical composition of stainless steel grades in this article in weight-percent.*

Common Name	UNS Number	Approximate EN Number Equivalent	Molybdenum	Chromium	Nickel	Nitrogen
Type 304/304L	S30400/S30403	1.4301/1.4307	-	18	9	-
Type 316/316L	S31600/S31603	1.4401/1.4404	2	17	11	-
2205	S32205/S31803	1.4462	3	22	5.5	0.16
2507	S32750	1.4410	4	25	7	0.27
254 SMO®	S31254	1.4547	6	20	18	0.2
AL-6XN®	N08367	-	6	20	24	0.2
Cronifer®1925hMo – alloy 926 INCOLOY®alloy 25-6MO	N08926	1.4529	6	20	24	0.2

Annual General Meeting 2002

The generous and lively hospitality offered by Molymet and Grupo Mexico, particularly an evening at Quinta Napoles hosted by Molymex and graced by the presence of the Sonora State Governor where tequila, music and dancing kept some delegates up until 3 a.m., was only matched by the high quality of the presentations (listed in the last Newsletter) at the AGM.

▲ Andreas Keller apparently not satisfied with just one dancing partner.

Hans and Gisela Imgrund. ▶

Thanks to Dieter Strathmann for the photos

Fifteen Thousand Metric Tons of Molybdenum for Nuclear Waste Containers in the US?

This article has been contributed by John Grocki of Advantage Resources (a consultant to IMOA)

Summary

The Yucca Mountain nuclear waste storage facility in the US State of Nevada is proposed to become the permanent centralized depository for all spent nuclear fuel and other high level radioactive waste in the US. The nuclear waste will be encapsulated in metallic storage containers which will be stored underground. The proposed construction materials for the storage containers are molybdenum containing, Type 316L stainless steel (2.2% Mo) for the inner container and nickel-base Alloy 22 (13.5% Mo) for the outer container.
The molybdenum containing materials were chosen for their corrosion resistance and expected longevity in the storage environment. As much as 15,000 metric tons of molybdenum would be necessary to build the 11,000 containers in the currently proposed material and design.

Background

The requirements of the Nuclear Waste Policy Act of 1982 directed the U.S. Department of Energy (DOE) to locate and develop sites for the permanent storage of spent nuclear fuel and high-level radioactive waste. Since 1987 that effort has been concentrated on Yucca Mountain, Nevada – a remote area approximately 100 miles (160 km) outside Las Vegas.

It is proposed that the spent fuel from nuclear power plants and other radioactive waste would be encapsulated in corrosion resistant storage packages and placed in tunnels under Yucca Mountain. The waste packages and the natural barrier of the mountain's rock formation are expected to keep the release of radioactive materials, either through ground water or atmospheric transport, at minimal levels. The containment must be functional for 10,000 years and beyond.

Before construction begins, the DOE must submit a request for licensing. This request will undergo a multi-year public review to insure all possible health and safety issues have been addressed. The DOE must prove that there is a reasonable expectation for the repository to maintain the health and safety constraints for the 10,000-year duration in order to receive a construction release. If this is accomplished, the DOE could begin construction on the site. The Nuclear Regulatory Commission has to grant a license before the site can receive any nuclear waste.

Natural and Man-Made Barriers to Leaching

The Yucca Mountain site was chosen for its geological and climate characteristics. The thick rock layers and the minimal rainfall would prevent any movement of radioactive materials out of the repository. The DOE has studied these characteristics with a multitude of test sites and experiments in and around Yucca Mountain for over twenty years. This included drilling a five-mile tunnel through the area where the repository would be located. Both surface and underground testing are continuing in order to validate the area's suitability for waste storage.

In addition to studying the natural barrier aspects of Yucca Mountain, the engineered, man-made barriers have also been extensively evaluated. A key factor in the design of the waste packages is the material selection. Materials were considered based on their corrosion resistant properties, mechanical strength, fabricability and commercial availability. As with the natural barrier, the man-made barriers must also provide 10,000-plus -years of protection for health and safety requirements.

The containers will be used to store a variety of radioactive waste, such as pressurized water reactor waste, naval fuel and vitrified high-level waste. Different size waste packages will be required for the different waste forms. The present design calls for the packages to be approximately 6 feet (1.8 m) in diameter with lengths ranging from 12 to 19 feet (3.7 to 5.8 m). An inner barrier will be constructed of 2-inch (51 mm) thick Type 316L (UNS S31603) stainless steel.
This barrier is designed to provide strength and bulk for structural stability. The outer barrier is presently designed as a 1-inch (25 mm) thick

nickel alloy (UNS N06022/EN 2.4602) cylinder, which will provide the long-term corrosion resistance. The two cylinders will be constructed from rolled and longitudinally welded plate. The inner UNS S31603 and outer UNS N06022 lids will be welded in place at both the top and bottom of the package.

A third barrier, drip shields, will be installed over the cylinders when they are placed in the tunnels. The drip shields will keep seeping ground water away from the canisters. Titanium – Grade 7 (UNS R52400) is being evaluated for this application.

Evaluation of Construction Materials

Testing programs to evaluate the long-term corrosion resistance and metallurgical stability of the materials have been ongoing for ten years. Corrosion testing to evaluate general resistance to repository environments will have been run for at least five years and some will continue for a much longer time. Some of the initial testing was done for up to 60,000 hours. Tests to evaluate susceptibility to localized attack, stress corrosion cracking and microbiologically-influenced corrosion have been and continue to be conducted. Short term testing to establish predictive corrosion susceptibilities are being compared to the longer term tests to help develop corrosion models for the 10,000-year extrapolation. While much of the testing is being done on base metal samples, weldments are also being tested.

As the waste decays, the temperature of the packages may over time increase to 350°F (177° C) and then return to near ambient temperature. To insure long term metallurgical stability of the candidate materials evaluations have been done on samples aged up to 40,000 hours. Exposure at temperatures up to and exceeding the 350°F (177° C) limit has been studied for effects on phase precipitations, long range ordering and the passive film oxide layer on the material's surface.

The testing completed to date has shown that the exterior barrier material UNS N06022 will provide excellent corrosion protection, maintain thermal stability and has suitable welding and fabrication characteristics. Other materials included in the test programs may also prove to be acceptable candidate materials.

Additional work is being done to develop the most appropriate fabrication techniques. This includes studying standard and advanced welding techniques such as vacuum electron beam welding. Surface enhancement treatments such as induction post weld heat treatments, laser peening and burnishing are being considered to remove residual stresses after welding. Finally, an inspection procedure will be developed to ensure the highest quality waste package assemblies are provided. Procurement documents for a test package will be issued in early 2003 with the first prototype unit to be completed in 2004.

Timeline

The preliminary schedule for the Yucca Mountain Project as of the end of 2002 is as follows:

NRC license application	**2003**
NRC construction authorization	**2006**
NRC license approval	**2010**
Begin acceptance of waste	**2010**
Complete waste storage	**2035**
Site closure	**2119**

Amount and Type of Material Required

If the project goes ahead as planned the delivery of some 11,000 waste packages would begin in 2010 and continue through 2035. The present plan is that 55% of the canisters will be the 21 Pressurized Water Reactor package type and 32% will be the 44 Boiling Water Reactor package type. These are the largest size waste packages. The remaining 13% of the packages will be smaller. If the construction materials remain as presently planned, UNS S31603 (17% Ni, 12% Cr and 2.2% Mo) and UNS N06022 (57% Ni, 22% Cr, 3% W and 13.5% Mo), the project will require approximately 180,000 and 92,000 tons (163,000 and 83,000 metric tons), respectively, of each alloy. This would translate into a requirement of 16 – 17,000 tons (14,500–15,400 metric tons) of molybdenum.

The UNS S31603 has already established itself for the inner barrier due to its superior corrosion resistance in the expected environment compared to the alternative UNS S30403, Type 304L stainless steel. While it is conceivable that additional materials will be qualified for the outer barrier, those potential materials will have moderately higher molybdenum contents than the UNS N06022.

Final Word...

The continuing research and development effort should ensure that this planned combination of natural and man made barriers will supply a safe nuclear waste storage solution for the thousands of years to follow.

Literature

This article has been compiled from the following documents:

Office of Civilian Radioactive Waste Management publications:

Overview: ***Yucca Mountain Project.***
DOE/YMP-0026, July 2002

What is nuclear fuel and waste?
DOE/YMP-0338, Oct. 2001

Nature and engineering working together for a safe repository.
DOE/YMP-0203, Oct. 2001

Providing a scientific and technical basis for repository decisions.
DOE/YMP-0202, April 2001

Volcanoes and Yucca Mountain.
DOE/YMP-0341, Oct. 2001

Studying the movement of rock and earthquakes.
DOE/YMP-0344, July 2002

The Exploratory Studies Facility.
DOE/YMP-0395, Oct 2001

Scientists look to nature for insight into how a repository would perform.
DOE/YMP-0205, June 2001

Matthew V. Veazey, November 2001. "Nuclear Waste Storage Plan Under Review", Materials Performance, Volume 40, Number 11, 14-16.

Thomas W. Doering and V. Pasupathi, January 2002. ***"Waste Package and Material Testing for the Proposed Yucca Mountain High-Level Waste Repository"****, INMM Spent Fuel Management Seminar XIX, January 2002, Washington, D.C.*

Proceedings from ***"Workshop #5 On the Fabrication, Welding and Corrosion of Nickel Alloys and Other Materials for Radioactive Waste Containers."*** *The Nickel Development Institute, October 16-17, 2002, Las Vegas, Nevada.*

Reference for Artwork:
Jeff Williams, Office of Civilian Waste Management, January 2002. "Program Briefing" INMM Spent Fuel Management Seminar XIX, January 2002, Washington, D.C.

Figure 1

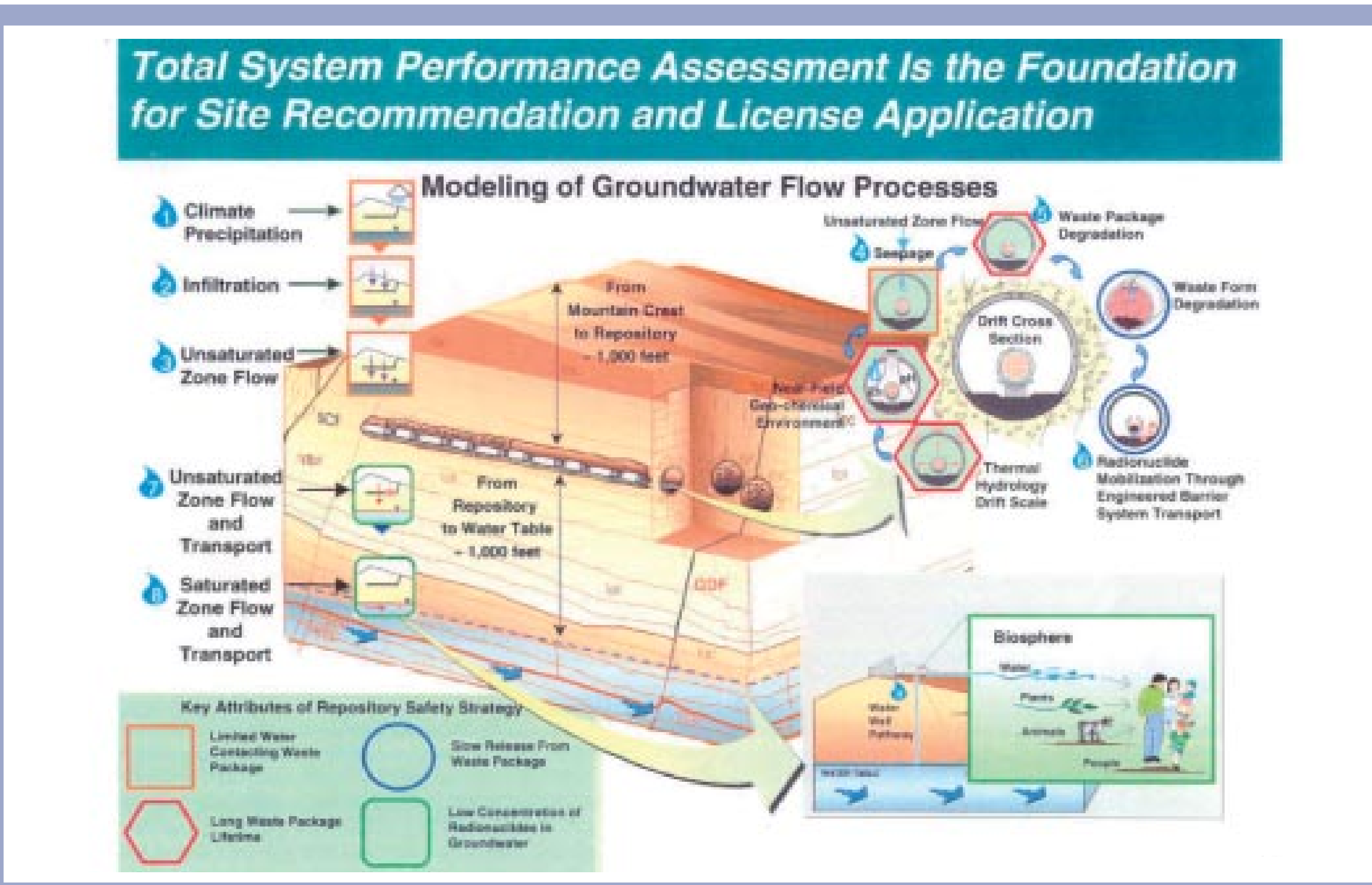

Figure 2

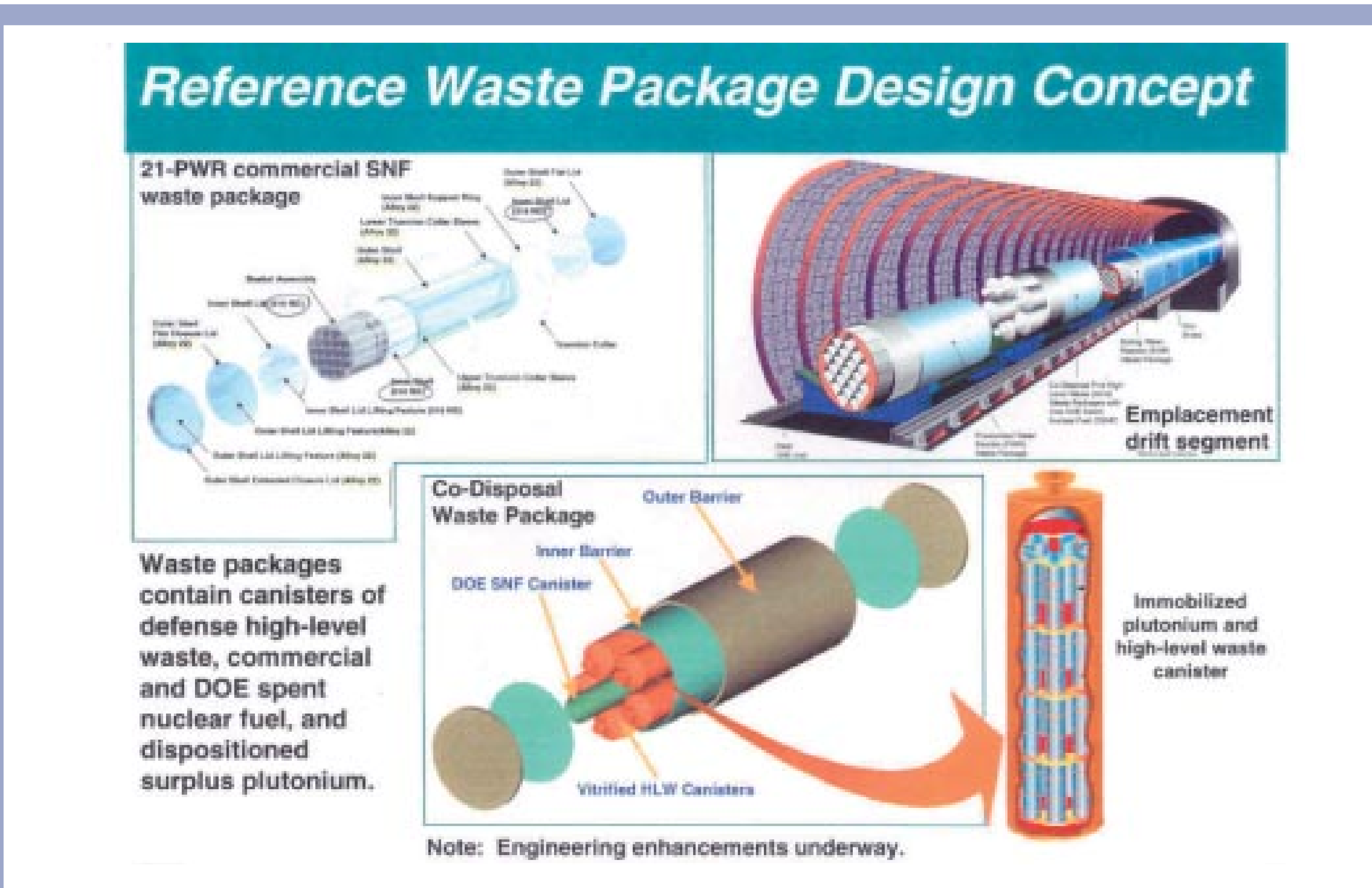

Figure 3

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