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AN OVERVIEW OF LOW TEMPERATURE SENSITIZATION

Michael J. Fox
R. Daniel McCright

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NOTICE

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PREFACE TO AN OVERVIEW OF LOW-TEMPERATURE SENSITIZATION REPORT BY M. J. FOX, CONSULTANT

R. D. McCright
Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory (LLNL) is responsible for high-level nuclear waste package development as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This project is part of the Department of Energy's Civilian Radioactive Waste Management (CRWM) Program, and is investigating the suitability of tuffaceous rocks at Yucca Mountain, Nevada Test Site for high-level radioactive waste disposal. The waste package effort at LLNL is developing multibarriered packages for safe, permanent disposal in a repository such as the one being considered at Yucca Mountain.

The physical, mechanical, and chemical stability of a metal barrier to survive the 300 - 1000 year containment objective is the paramount technical issue in selecting a suitable container material for geological disposal of high-level nuclear waste. Austenitic stainless steels serve as the reference container materials in the conceptual design for nuclear waste packages for a comtemplated geological repository in tuff located in Yucca Mountain at the Nevada Test Site. The corrosion resistance of candidate container materials in the anticipated repository environment is the focus of an experimental program to establish a data base on which the final material selection will be made and from which models to project the long-range corrosion performance will be developed.

One major problem in use of austenitic stainless steels is susceptibility to developing a sensitized microstructure when exposed to relatively high process temperatures for short periods of time. Chromium-rich carbide phases precipitate largely in the grain boundary region and impoverish the local area of chromium. The resulting chromium-depleted area is then more susceptible to localized attack, because the steel in this local area does not contain sufficient chromium to maintain a stable, protective, passive film. The low carbon grades of stainless steel (such as 304L) were developed to resist sensitization by tolerating a much longer time at a given temperature before carbide formation occurs. A particular concern in geological disposal of nuclear waste packages is development of a sensitized microstructure over the long containment period (100's of years) at modest temperatures (100-300°C) which are produced in the container by decay of fission products in nuclear waste.

Dr. Michael Fox, an independent consultant, was retained to compose the attached report to assess the possibility of the occurrence of a sensitized microstructure in 304L stainless steel containers. As sensitization effects may accumulate from previous high temperature processes, Dr. Fox was asked to consider the influence of fabrication and welding on the possible subsequent development of sensitization during geological storage at lower temperatures. Additional potential sources of sensitization are the casting of vitrified reprocessed waste forms in stainless steel canisters (Defense and Commercial High Level Waste - DHLW and CHLW). During his previous employment at General Electric and at the Electric Power Research Institute (EPRI), Dr. Fox published papers on low temperature sensitization, particularly as the phenomenon affects the stability of Type 304 stainless steel in the Boiling Water Reactor (BWR) coolant environment. Type 304 stainless steel is used for piping carrying high-temperature, pressurized water (ca. 290°C) and steam in the BWR. Sensitization effects in the heat-affected-zones around the welds in the piping have led to intergranular stress corrosion cracking (IGSCC) problems which mandated shut-downs for inspection of crack development. This has been a costly problem for the utilities owning BWRs and much work has been sponsored by EPRI in this country and by similar organizations in other countries. Much of the work has centered on understanding different aspects of the sensitization phenomenon and on developing remedial measures. Dr. Fox's access to this information - much of which is not yet published in the open literature - was most helpful.

A good deal of the EPRI-sponsored work concerns alternative materials to 304 stainless steel for replacement of the piping in some existing BWRs and for construction of new generation BWRs. These alternative materials include the low carbon grades of the basic 18-8 stainless steels, special premium grades with controlled levels of carbon, nitrogen, and other interstitials, and the more highly alloyed stainless steels. These materials are also being considered for nuclear waste containers in a tuff repository. Recent papers (1, 2) detail the selection of reference and alternative container materials in the conceptual design stage of the nuclear waste package. These papers give an outline of all the corrosion concerns with these materials and discuss a test plan for resolution of these concerns.

Dr. Fox's comments and recommendations are based on information about the conceptual design which was available to him in December 1983. Some of this information is preliminary in nature and is subject to modification. Therefore, the reader should keep the following points in mind:

1. The discussion on temperatures attained in a canister during the glass casting operation is based on information available from processing defense waste at Savannah River Laboratory. Canister temperatures were measured and reported during glass pouring operations (3, 4). These measurements indicated a peak temperature of 550°C (see Figure 1). In a more recent private communication, subsequent temperature measurements showed that a maximum measured temperature of only 460°C occurred. During this most recent operation, the pouring rate was kept low throughout the pouring operation, while the rate was speeded up toward the end of the previously reported determinations. All other factors being the same, if the canister surface peak temperature is reduced, a sensitized microstructure is less likely to develop. This point is illustrated in Figure 3 where the times and temperatures occurring during a DHLW-simulated pouring operation are superposed on laboratory data generated by Briant on sensitization of cold-worked 304L stainless steel coupons. The area to the left and below the line for Briant's data corresponds to the time-at-temperature conditions which produce a sensitized microstructure. Figure 3 indicates that reducing the peak temperature is beneficial in retarding sensitization. On the other hand, the work performed so far at SRL has considered a limited number of thermocouple locations for determining temperature. The possibility arises that higher local temperatures occur for short periods of time. A possible location of a thermal spike is at the canister bottom where the first part of the molten glass strikes the canister.

All of these reported temperatures were determined for non-radioactive glass. The "hot" material will increase the ambient temperature to which the glass eventually cools and this thermal source will tend to prolong the period at which a given temperature prevails at a point in the canister. This thermal source is probably negligible in DHLW packages because of the low power loadings but it may be a consideration in the CHLW packages (2.2 kW for 10-year old waste). From the analysis shown in Figure 3, increasing the time at a given temperature increases the susceptibility of the alloy to develop low temperature sensitization.

2. The geological storage temperature will have a large bearing on whether a sensitized microstructure occurs. As illustrated in Figure 4, the storage cooling curve when superposed on Briant's data (a "worse case") for laboratory-induced sensitization indicates that the higher the canister temperature, the greater is the occurrence of falling into the sensitized zone. Figure 4 shows that temperatures exceeding 280°C for the first ten years after emplacement are detrimental. The actual storage temperature depends on many factors - related to waste package design (e.g., package dimensions, type of waste, use of packing material, power loading per canister) and related to repository considerations (e.g., thermal conductivity of rock and other barrier materials, vertical vs. horizontal emplacement, areal loading of waste packages) - so that any predicted thermal history must be qualified. The thermal decay curves given in Figure 2 are intended to be representative of each kind of waste package. More recent calculations on canister surface temperatures (5) generally indicate lower maximum values for vertically emplaced CHLW (230°C) and BWR Spent Fuel (SF) (240°C) packages than the values indicated in Figure 2. Packages placed near the outside of the package array in the repository develop even lower surface temperatures. Many decisions on the design and repository arrangement are open issues; from the point of view of preventing a sensitized structure, designing the waste package to maintain as low a temperature as possible on the container surface is desirable (see Figure 4).

3. From the above discussion, it follows that the CHLW canisters should have the greatest susceptibility toward sensitization because of the combination of high temperatures developing during the glass casting operation and the high storage temperatures produced by the initially high inventory of

radionuclides. The SF packages would have the least susceptibility toward sensitization provided that the storage temperature can be maintained on the "low side" and the canister stock has been annealed and stress relieved after fabrication and welding. With the possible exception of the final closure weld on the SF canister, microstructural and residual stress effects from previous operations can be appropriately modified and reduced. The susceptibility of DHLW to sensitization should fall in between that of the CHLW and that of the SF packages. The peak storage temperature for DHLW packages is 145°C (5), which is clearly beneficial in retarding sensitization; but high peak temperatures and residual stress produced during the glass casting operation may favor subsequent sensitization. Keeping the peak canister temperature low during glass casting is beneficial. Recent private communications from Savannah River indicate that a significant part of the initial oldest defense waste to be disposed of has a power load much less than the value used to calculate these temperatures (60 watts vs 680 watts). Thus, even lower temperatures should occur with the result of a decreased susceptibility toward low temperature sensitization.

The lower environmental temperatures surrounding DHLW waste packages may produce a counter and detrimental effect, as "wet" conditions may develop after a much shorter storage time. As long as unsaturated (with respect to condensation of water) conditions dominate the canister environment, even a highly sensitized microstructure should not exhibit an adverse performance because of the absence of an electrolyte. However, once moisture condensation or water intrusion is possible, then corrosion cells can be established. Given the right environmental conditions, a sensitized microstructure can then result in intense localized attack.

4. This report was not intended to consider environmental effects on the premature failure of a canister with a sensitized microstructure. The experience with sensitized 304 stainless steel pipes cracking in the BWR coolant environment (high purity water, 0.2 ppm dissolved oxygen in the steady state) indicates that quite mildly oxidizing conditions can provoke attack. Some parallel situations can be drawn between the BWR environment and the expected environmental conditions prevailing in a repository in Yucca Mountain. The vadose water which would be found in the vicinity of the

repository is expected to be nearly saturated with oxygen. Nitrate ion (5-6 ppm level) is found in J-13 well water which is believed representative of the vadose water percolating through the unsaturated zone. These dissolved species give the water an oxidizing characteristic compared to the redox potentials of most metals. Further, gamma radiation from the waste form generates radiolysis reactions in the water which will likely make it more oxidizing. Thus, it appears that a canister with a sensitized microstructure will be vulnerable to intergranular corrosion or to intergranular stress corrosion cracking when it contacts this water. (A large portion of the metal testing program is aimed at evaluation of these phenomena.)

Mitigating environmental factors are present and need to enter into the discussion. For most spent fuel packages, the temperatures should remain above the boiling point of water for most of the 1000-year containment period. However, for 10-year old CHLW (2.2 kW load) the temperature at the container surface reaches the boiling point of water (95°C) in about 200 years after emplacement; and for DHLW packages, after about 150 years (680 watt power load). The power load in DHLW packages depends on the age of the sludge and the age of the supernatant. A range of different power loads is possible, as discussed in Reference 3, with the 680 watt load being among the highest considered. Lower initial power loads in packages containing older waste would result in this temperature being reached in shorter time periods. Even when the canister surface temperature reaches 95°C, water will condense at locations in the repository which are cooler than the relatively hot canister. Thus, aqueous corrosion can occur only when accumulation of water allows immmersion of parts of the canister for significant periods of time. These circumstances are likely to be rare in the unsaturated Topopah Spring hydrologic setting. Also, the radiation field intensity falls off with time. For CHLW packages the radiation field drops to 10% of its approximate 10^5 rads/hr initial value after 100 years. The radiation field around a DHLW package is about two orders of magnitude lower. Thus, when liquid water in the immediate package environment is a possibility, the radiation field is considerably weaker and radiolysis-induced reactions may be negligible.

With consideration of both environmental and process history/sensitization effects, the CHLW package canister is predicted to be the most susceptible to IG/IGSCC forms of corrosion once condensed water contacts the package. One way to minimize a premature breach of the canister by these forms of corrosion is to overpack the CHLW canister. The overpack can be fabricated (with appropriate stress reliefs and solution annealing, if needed) so that a minimum of residual stress remains in the emplaced outer container.

5. All of the long-term low-temperature sensitization predictions are based on extrapolations of observations made by exposure of a sample to an intensely corrosive medium to accelerate the largely intergranular attack of the chromium-depleted areas. This statement holds for the ASTM A262 standardized tests and for the relatively new electrochemical polarization reactivation (EPR) technique, which are discussed in the report. These accelerated tests indicate that attack occurs because particles above a critical size have been produced. Chromium carbides are produced by a nucleation and growth mechanism. There may be a temperature below which growth of previously initiated carbides will be so slow so that for all practical purposes - even in long-term (thousand-year) containment - no growth of the carbide occurs, and the chromium in solid solution around the carbide is nearly the same as the bulk composition in the steel. The similarity in chromium content would eliminate the driving force to initiate the localized attack. Thus, the DHLW package may have a great deal of resistance to low-temperature sensitization despite the process history of the canister.

6. The report recommends that types of stainless steel other than 304L be pursued as container construction materials. It is interesting to note that 316NG (nuclear grade-extra low carbon, higher nitrogen version of 316L) is the recommended material for replacement of 304 piping in the BWR. The alloy is less susceptible to IGSCC in the BWR environment than comparable premium 304L grades. A decision on whether to continue 304L stainless steel as the "reference material" will be made with the selection of materials for the "prototype design", which is the next level of design effort. There are other corrosion concerns in addition to sensitization-induced forms of corrosion to factor into this decision. In the meantime, the experimental program is proceeding with emphasis on corrosion testing of 304L as well as 316L and 321 stainless steels and alloy 825 (high-nickel alloy). The intent of the program is to survey the different possible corrosion failure modes for these alloys and to test for these forms of corrosion in the expected

repository environmental conditions and under adverse "what if" circumstances. Intentionally sensitized specimens, cold-worked specimens, stressed specimens, welded specimens, and - combinations of these conditions - are currently undergoing a variety of tests (including four-point-loaded bent beam, C-ring, U-bend, slow strain rate, fracture mechanics specimens).

Efforts will continue to monitor time-temperature histories developing during actual pours of vitrified waste forms with measurements at more locations in the canister. Also, stress measurements and stress changes will be measured by application of strain gauges at different locations in the canister. Additional design work and improvements in the heat transfer code used to calculate projected thermal patterns in the repository will supply additional information on predicted temperature histories for the different waste packages.

References

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Prepared for
Lawrence Livermore National Laboratory

by

Michael Fox, Ph.D.
7490 Stanford Place
Cupertino, California 95014
(408) 996-0994

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OVERVIEW OF LOW TEMPERATURE SENSITIZATION

1.0 Introduction

1.1 Nature of the Problem

The U.S. Department of Energy (DOE) is investigating a possible underground nuclear waste repository in the volcanic rock deposits of Nevada. A proposed method for waste storage involves the encasement of nuclear waste in molten borosilicate glass (Defense High Level Waste and Commercial High Level Waste). The molten glass and waste mixture (1050°C) is poured into stainless steel canisters where it is allowed to cool and solidify. Through contact with the molten glass, the stainless steel canisters will be momentarily heated to about 1050°C and will immediately begin to cool by convection to a temperature near 300°C. The time of exposure between 1050°C and 300°C may be on the order of seconds, minutes or hours, depending on the specific location within the canister walls (bottom, side, inside, or outside). The canister and glass do not cool rapidly below 300°C due to the continued production of heat by the radioactive decay of the nuclear waste. Some forms of glass-solidified nuclear waste will require more than 1000 years to cool from 300°C to 100°C, and all forms will be over 100°C for many hundreds of years.

In view of the long-term nature of nuclear waste storage, the Lawrence Livermore National Laboratory is investigating the long-term corrosion resistance of the stainless steel canisters that will contain the glass-solidified nuclear waste. At the conceptual design level, the reference material for fabricating these canisters is Type 304L stainless steel. This general class of materials, the austenitic stainless steels, are very resistant to corrosion in the solution annealed condition, hence the name "stainless" steels. However, when stainless steels are exposed to heat treatments between 550°C to 800°C, they become susceptible to various forms of localized corrosion, including intergranular attack (IGA), intergranular stress corrosion cracking (IGSCC), and (sometimes) transgranular stress corrosion cracking (TGSCC). When a stainless steel is made susceptible to corrosion by such heat treatments, the stainless steel is said to be "sensitized", and the heat treatments are referred to as "sensitizing" heat treatments. Section 1.2 discusses the phenomenon of "sensitization" and outlines the reasons to suspect that canisters made from Type 304L stainless steel may not be suitable for the long-term storage of nuclear waste.

1.2 Definition of Sensitization and Low Temperature Sensitization (LTS)

The phenomenon of sensitization has been reviewed extensively by others (Cowan and Tedmon, 1973) and will not be described in detail. Briefly, an alloy is said to be "sensitized" if it is more susceptible to intergranular or transgranular attack than a nonsensitized sample of the same alloy. This sensitized condition is usually the result of isothermal exposure in the 550°C to 800°C temperature range. The most widely accepted explanation for sensitization is the chromium depletion theory (Bain, Aborn and Rutherford, 1933), which attributes the increased susceptibility to the formation of chromium carbide particles and the accompanying depletion of chromium from the adjacent matrix. Chromium is responsible for the corrosion-resistant (or "stainless") quality of stainless steels, and the local depletion of chromium can lead to localized corrosion.

The sensitization that occurs upon welding stainless steel is limited to a region adjacent to the weld and is referred to as the weld heat affected zone (HAZ). In most cases, the degree of sensitization that occurs upon welding is not severe. However, it has been shown (Povich, 1978) that increased sensitization can subsequently develop at temperatures well below the normal sensitization temperature range if chromium carbide nuclei are present. The phenomenon has been referred to as low temperature sensitization (LTS).

The potential relevance of LTS to nuclear waste storage may be described as follows: when Type 304L stainless steel canisters are welded, carbides are nucleated in the weld heat affected zone (HAZ), but produce very limited sensitization. However, after many years at nuclear waste storage temperatures, the degree of sensitization may increase via LTS to enhance the possibility that stress corrosion cracking would occur.

Extensive research has been conducted in laboratories throughout the world on the nature of LTS in stainless steel. The results show that LTS is a nucleation and growth phenomenon: the chromium carbide particles are nucleated at higher temperatures (500-800°C) and then continue to grow at lower temperatures (below 550°C) by the diffusion of carbon and chromium to the carbide particles. Since the diffusion of carbon (interstitial) is fast relative to the diffusion of chromium (substitutional), the rate-limiting step for LTS is usually the diffusion of chromium. LTS has been found to obey an exponential temperature dependence with activation energies ranging from 40 to 70 Kcal/mole, depending on the degree of cold work and on the test method used to measure sensitization. An activation energy of 70 Kcal/mole corresponds to the diffusion of chromium through the bulk stainless steel, while activation energies of 40 Kcal/mole corresponds to diffusion of chromium along grain boundaries or dislocation pipes.

The high-temperature nucleation of carbides can occur upon welding or any other brief high-temperature exposure. In the case of nuclear waste canisters, the high-temperature exposure could occur upon welding the canister during fabrication, or as the result of the molten (1050°C) glass/waste mixture that is poured into the canister.

Temperature measurements performed at Savannah River on "cold" defense waste indicate that the outside walls of the canister do not surpass 550°C during the molten glass pouring; however, the inside surface of the canister wall would attain some higher temperature. The glass leaves the melter at 1050°C, and cools about 25°C for each foot of drop into the canister. The drop is about ten feet so that the glass strikes the canister bottom at about 700°C. Therefore, a time-dependent temperature gradient must exist through the canister wall. Also, the bottom of the canister, if in contact with a supporting floor, could be insulated from rapid cooling. Therefore, the outside surface of the bottom of the canister could be exposed to a temperature range that would nucleate chromium carbide particles. This would be particularly true if the floor was not a conductor of heat. Figure 1 illustrates the time-temperature behavior as measured at the outside surface of the canister. No data are currently available on the time-temperature behavior as a function of wall thickness.

It has also been shown that cold work will lower the temperature needed to nucleate carbides. This data is described in section 3.1. Therefore, if the Type 304L canister is sufficiently cold worked, carbide nucleation could occur throughout the canister walls during the pour and long-term storage.

The long-term low temperature exposure of the nuclear waste canisters can come from two sources: the natural cooling of the molten glass/waste form mixture and the continued generation of heat from the radioactive decay of the nuclear waste. For defense waste, the canister cools to ambient temperature within 24 hours, as shown in Figure 1. The process for fabricating and casting commercial high-level glasses is not yet as developed as the process for defense high-level waste although similar temperature profiles would be expected during cooling. Essentially ambient temperatures prevail on the canister surface during interim storage (before emplacement in the repository), because the natural convection in the atmosphere dissipates heat internally generated by the waste form in the canister. Once the filled canister is emplaced in the repository, however, the canister temperature rises and then slowly decays because of the relatively poor heat transfer of the geological formation. Calculated, comparative canister surface temperatures which develop for the different kinds of waste packages are shown in Figure 2. The actual temperature-time profile after emplacement will depend on several factors in the waste package design and in the repository design. From the point of view of low-temperature sensitization, the very long times (10s to 100s of years) when the canister surfaces are in the approximately 100-300°C temperature range coupled with the previous time-temperature history may significantly influence metallurgical reactions in the alloy.

1.3 The Purpose of this Report

This report is a comprehensive literature review on LTS. The purpose of the review was to determine if LTS-related metallurgical changes can occur in commercial Type 304L stainless steel within the times and temperatures associated with nuclear waste storage. Any such changes could affect the long-term corrosion resistance of the currently designed waste storage canisters. However, it is not the purpose of this review to determine if corrosion will or will not occur. That determination would require additional specific experimental work.

2.0 Background Information

2.1 Source of Data and References

A problem that has plagued the Boiling Water Reactor (BWR) Industry for the past ten years is the intergranular stress corrosion cracking (IGSCC) of Type 304 stainless steel pipe welds. Three conditions are needed for IGSCC of stainless steel to occur: (1) a tensile stress, (2) an environment that will facilitate IGSCC, and (3) a sensitized microstructure. As a result, a considerable amount of research (over $100 million) has been conducted on how each of these factors can be used to cause or prevent IGSCC. About 10 years ago, when the IGSCC problem first became apparent, some serious consideration was being given to the low-temperature (500°C) stress relief of Type 304 stainless steel pipe welds. In small-scale tests at General Electric, it was shown that a significant level of stress relief could be accomplished by a 500°C/24-hour heat treatment. Furthermore, it was not believed that this heat treatment would cause any sensitization. However, Povich showed that a 500°C/24-hour heat treatment would severely increase the degree of sensitization via low temperature sensitization (LTS). The phenomenon of LTS is discussed in Section 1.2. Furthermore, Povich (1978) went on to establish that LTS can occur at even lower temperatures (350°C) and predicted that an LTS-enhanced susceptibility to IGSCC could occur at BWR operating temperatures (288°C) within 10 to 20 years. This, in turn, led to international interest in LTS research. The Electric Power Research Institute (EPRI) has funded a significant amount of LTS-related research and has organized LTS workshops and IGSCC seminars.

Much of the data and material reviewed for this report comes from the BWR industry and EPRI-sponsored reports, workshops and seminars. While the focus of tnese sources is on IGSCC in BWRs, the information pertaining to LTS is directly applicable to the purpose of this report, which is to determine if LTS-related metallurgical changes can occur in commercial Type 304L stainless steel within the times and temperatures associated with nuclear waste storage.

2.2 Test Methods, Terminology and Abbreviations

LTS Low Temperature Sensitization

LTS generally refers to a heat treatment below 500°C. However, an LTS heat treatment of 500°C/24 hours became common, and frequently, "LTS" (if not otherwise defined) means 500°C/24 hours. Generally, this heat treatment will not induce further sensitization unless chromium carbide particles are already present from a prior higher temperature exposure. It has also been observed that 500°C/24 hours is a screening test for LTS susceptibility. If 500°C/24 hours does not increase the degree of sensitization, then the material is probably not susceptible to LTS or does not have chromium carbide nuclei.

A262E ASTM Designation A262-68 Practice E

A262E is the acid/copper sulfate test. It consists of a boiling solution of sulfuric acid and copper sulfate. The A262E test is said to attack chromium-depleted regions (less than 12%) in stainless steel (Cowan and Tedmon, 1973). The results of A262E are usually reported as some measure of crack depth, or the loss of some mechanical property due to the corrosive attack. If stainless steel is severely sensitized, the A262E test can remove entire grains and even reduce a small sample to powder. The copper sulfate maintains the metal/solution interface potential in the passive region so that only chromium-depleted regions are attacked. Dilute sulfuric acid alone will completely dissolve stainless steel.

A262A ASTM Designation A262-68 Practice A

A262A consists of passing a specified amount of electric current through a test sample submerged in a solution of oxalic acid. It is also referred to as the Oxalic Acid Etch Test. Results are reported as the way that the metal surface appears after the test: step, ditch, or dual (both step and ditch). A262A is said to dissolve chromium carbide particles present at the grain boundaries (Cowan and Tedmon, 1973).

Huey Test   ASTM Designation-A262-68 Practice C

The Huey Test consists of exposing a test sample in boiling 65 wt% nitric acid. Results are presented as the percent weight loss per unit area. This is a very severe test that is sensitive to chromium depletion, chromium carbides and sigma phase.

EPR   Electrochemical Potentiokinetic Reactivation Test

In the EPR Test, a specimen is subjected to 2 potential sweeps in a deaerated solution of sulfuric acid and KCNS. A reactivation peak is formed on the reverse current-potential sweep, and the area under this curve is proportional to the degree of sensitization (DOS). This is basically the General Electric version of the EPR Test. There is also a Japanese version (Nakagawa et al., 1983) that uses the ratio of peaks obtained in the forward and reverse current-potential sweeps as the measure of the DOS.

CERT   Constant Extension Rate Test

CERT is also known as the Slow Strain Rate Test (SSRT). It consists of applying a constant extension rate to a specimen in a test environment. CERT is an accelerated screening test for stress corrosion cracking (SCC). Since CERT applies excessive stresses and strains, it is a reliable test to screen either the environment's ability to produce SCC or the susceptibility of the specimen to SCC. If the CERT environment is known to facilitate SCC, then CERT becomes a screening tool for the susceptibility of the material to SCC. This is generally how CERT is used in LTS-related studies. Therefore, CERT can be used to detect LTS-related changes that lead to increased susceptibility toward SCC.

WOL/CT   Wedge Open Loaded/Compact Tension

WOL/CT refers to either of these standard fracture mechanics tests used to measure crack growth. WOL/CT is similar to CERT in that very high stress intensities can be created. When a WOL/CT environment is used that is known to produce SCC, WOL/CT becomes a tool to detect the test material's susceptibility to SCC.

CBB Crevice Bent Beam Test

The CBB Test consists of placing a coupon of test material in a curved vice-like fixture that bends the specimen. An artificial crevice is made on the tensile side of the specimen by introducing a piece of graphite wool. The sandwich of graphite wool, specimen and CBB fixture is then placed in a test environment, usually a high-temperature aqueous environment. Results are reported as the depth of SCC attack after the specimen is removed and examined by UT or metallography. The Japanese developed the CBB Test as a tool to study IGSCC in BWRs. Therefore, the aqueous environment most often used for this test is high-purity water at 250°C containing dissolved oxygen.

CPT Creviced Pipe Test

The Creviced Pipe Test is a full-scale version of the CBB Test. An artificial crevice is made from graphite wool and a mandrel inside of a full-scale pipe weld. No external stress is created in the CPT. The driving force for SCC is the residual stress of the pipe weld. A version of this test could be created for the accelerated SCC testing of nuclear waste storage canisters. The crevice can be made on the outside or the inside of the canister.

Other acronyms and abbreviations include:

TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
AES	Auger Electron Spectroscopy
SEM	Scanning Electron Microscopy
SCC	Stress Corrosion Cracking
IGSCC	Intergranular Stress Corrosion Cracking
TGSCC	Transgranular Stress Corrosion Cracking
AW	As-Welded
NG	Nuclear grade (low carbon (.02%) plus nitrogen)
LN	Low carbon (.03%) plus nitrogen
PTL	Pipe test loaded

3.0 Review of Key Reports and Papers

Over 50 reports were reviewed. Of these, 15 contained information on low carbon stainless steel, and 9 contained data pertinent to the low temperature sensitization (LTS) of low carbon stainless steel. All of the references are listed in Section 6.0 of this report. The nine most significant reports are discussed and summarized in this section.

3.1 Author: Briant, C. L.

Title: Effects of Nitrogen and Cold Work on the Sensitization of Austenitic Stainless Steels.

Reference: EPRI NP-2457, Project 1574-1, Final Report June 1982.

Materials: 304, 304L, 304LN, 316, 316L, 316LN.

Carbon: .013-.078%

Test Methods: A262E, A262A, Huey, TEM, SEM, Auger.

Summary:

This study uses 15 specially prepared laboratory heats of stainless steel and three commercial heats of stainless steel to study the effects of C, P, S, N, Mn, Si, cold work, and heat treatment on sensitization. The major finding of this study is that martensite (induced by cold work) can greatly accelerate sensitization and LTS in Type 304L stainless steel. In one series of experiments on a cold worked high purity laboratory heat of Type 304L (.028% C), susceptibility to A262E is predicted to occur somewhere between 1.3 and 6.8 years at 288°C. Since the temperatures of some waste packages during the first 10 years of storage may reach the vicinity of 280°C, this paper alone raises concern about the possibility of an LTS-enhanced susceptibility occurring within the times and temperatures associated with nuclear waste storage.

Several additional aspects of Briant's work need to be pointed out:

- Both TGSCC and IGSCC were observed, with TGSCC being predominant at higher heat treatment temperatures and IGSCC at lower temperatures.

o Severe cold work was used in the LTS experiments. The samples were stressed to near their ultimate tensile strengths to introduce cold work and martensite. This degree of cold work is unrealistic if one considers the likely bulk deformation of a nuclear waste storage canister. However, local cold work to this extent frequently does occur upon grinding or grit blasting. It is also noted that "abrasive cleaning" is planned to remove radioactive debris from the outside of the nuclear waste storage canister CHLW and DHLW). This abrasive cleaning could introduce severe cold work in a thin surface layer of the canister.

o No high-temperature carbide nucleating heat treatment was required for the LTS of the severely cold worked 304L.

o The 304L used in this study was a high purity laboratory heat. Therefore, there is little possibility that other impurities contributed to the LTS-enhanced susceptibility.

o The study also shows that even without cold work, the low carbon stainless steels are susceptible to sensitization when sufficiently heat treated. For example, 304L with .028% C is susceptible to A262E after 1-10 hours at 650°C. These are times and temperatures that could be encountered on the inside of the canister walls during the initial cool down of the molten glass/waste mixture after it is poured into the waste canister. Of course, when the same material is cold worked, it can sensitize in minutes or seconds at 650°C.

3.2 Authors: Andresen, P. L., et al.
Title: Basic studies on the Variabilities of Fabrication-Related Sensitization Phenomena in Stainless Steel.
References: EPRI NP-1823, Project 1072-1, Final Report, May 1981.
Materials: 304, 304L, 316, 316L, 347, XM-19
Carbon: .012-.077%
Test Methods: A262E, A262A, CERT, TEM, STEM, weld simulation
Summary:

There are two sections of Andresen's report relevant to the LTS of low carbon stainless steel: Section 3.3 of Part I is a thermodynamic and kinetic analysis of LTS, and Part II is an experimental study of the influence of thermal strain on LTS. The thermodynamic and kinetic analysis in Part I concludes that the Arrhenius extrapolation provides the most probable estimate of sensitization times at lower temperatures, and if anything, will underestimate the DOS that will occur. Specific theoretical equations and plots are presented.

Part II describes an experimental study on weld simulation using six heats of 304 stainless steel and one heat of 316 stainless steel. The carbon content varied from .030% to .077%. The study also investigated six heats of 316L and one heat of 304L with carbon contents in the .012-.022% range. The method of investigation involved weld simulation using cooling rates and strain as variables. The results of the cooling rate studies on 316L showed that 316L can be attacked by A262A if heated to 800°C and then allowed to cool at a rate slower than 0.1°C/sec. The only material that was not attacked by A262A in this cooling rate study was a heat of 304L that contained .012% C, which was the lowest carbon content of all the heats studied. None of the304L or 316L heats were attacked by A262E under the same conditions that produced attack by A262A. This is an indication that chromium carbides were formed, but chromium depletion (below 12%) did not occur.

The experiments on 304 and 316 with carbon contents between .030 to .077% showed that cooling rates between .1-.01°C/sec are needed to bring about susceptibility to A262E.

In all experiments, prior cold work (or strain imposed during weld simulation) increased the susceptibility to sensitization and LTS. This is consistent with the findings of Briant, discussed in Section 3.1. However, the strains imposed by Andresen are not as severe as those imposed by Briant.

The slow cooling rates that are needed to produce sensitization in 304L and 316L are not normally encountered in conventional welding practices. However, in the storage of nuclear wastes, slow cooling rates may be encountered during the initial cool down of the molten glass/waste mixture after it is poured into the waste canister.

3.3. Author: Alexander, J. et al.
Title: Alternative Alloys for BWR Pipe Applications
Reference: EPRI NP-2671-LD, Project T11101, Final Report October 1982
Materials: 304, 304L, 304NG, 316, 316L, 316NG, 347, CF-3, XM-19
Carbon: .009-.079%
Test Methods: A262E, A262A, EPR, CERT, CBB, PTL, TEM, STEM, SEM, AES
Summary:

This report describes an extensive experimental qualification program for alternate BWR piping alloys. In general, all of the alternate alloys were found to be sufficiently superior to regular Types 304 and 316 stainless steels, and therefore suitable for BWR piping. However, the report also shows that 316L and 304L are susceptible to sensitization if exposed to a sufficient heat treatment, such as 600°C/100 hours. Under these conditions, sensitization was confirmed by A262E, TEM and STEM. While 600°C/100 hours is beyond the range of times and temperatures of practical interest, it should be kept in mind that these samples were not previously cold worked, and it is significant that any sensitization at all can occur. In CBB tests described in Section 6.5 of the reference, cold work is shown to produce both IGSCC and TGSCC. In this case, the sensitization (677°C/8 hours) determined whether the cracking was intergranular (sensitized) or transgranular (non-sensitized). The role of LTS is masked because weld simulation was used prior to LTS. The weld simulation exposes the sample to temperatures above 1000°C, which anneals most of the prior cold work, thereby reducing the effect of subsequent LTS. The important point here is that one should not become overconfident based on sensitization tests that do not employ some degree of cold work, since any practical application is likely to involve cold work.

This reference also contains other experimental evidence that the low carbon stainless steels are not immune to SCC. Unfortunately, it is difficult to separate the role of LTS since all samples (of interest here) were given an LTS (500°C/24-hour) heat treatment. Section 4.5 of the reference describes pipe tests in high-temperature water containing 20-184 ppm chloride in which IGSCC occurs in both 304NG and 316NG pipe welds. This illustrates an important point. To determine whether it is possible for SCC to occur in any given application, such as nuclear waste storage or BWR piping, it is necessary to perform accelerated SCC tests in the most realistic/worst environment that may occur.

Appendix D of the reference describes WOL/CT experiments in which severe IGSCC is observed in 304, 304NG, 316L, 316NG, 347, and XM-19. The authors of Appendix D comment that unsensitized samples behaved similarly, but no experimental data or metallography is presented. The authors suggest that the severe IGSCC is due to crevice chemistry inside the WOL/CT fatigue precrack. However, there were also clear indications of IGSCC originating from a relatively stress-free and crevice-free surface of a 316L WOL/CT specimen. All of these WOL/CT experiments were performed in 288°C high purity water containing 8 ppm of dissolved oxygen.

Section 6.3 of the reference describes EPR experiments on 304, 304NG, 304L, 316L, and 316NG. All of the samples were removed from welded pipes and then subjected to long-term, low-temperature (677°C-288°C) heat treatments to determine the likelihood of LTS. The results are sufficient to make Arrhenius plots for 304 and 304L. However, the lower temperature heat treatments on 304NG, 316L, and 316NG were stopped too soon to make meaningful Arrhenius plots. Surprisingly, Type 304L would be expected to become sensitized within 20 to 40 years at 288°C.

3.4 Author: Nakagawa, Y. G.
Title: 1st LTS Study and 2nd LTS Study
Reference: Private Communications - 1978, 1979
Materials: 304, 304L, 316L, 347
Carbon: .026-.04%
Test Methods: Weld Simulation and A262E
Summary:

These papers specifically investigate the possibility of LTS in types 304, 304L, 316L, and 347 stainless steels. The method of study involves weld simulation with torsional strain, followed by LTS heat treatments. The LTS heat treatment is limited to 500°C/24 hours for 304L, 316L and 347. The LTS heat treatments for the 304 stainless steel ranges from 500°C to 400°C. The results show that 304L is susceptible to A262E after weld simulation plus LTS.

The papers also describe the equations needed to calculate the chromium concentration as a function of the distance from the chromium carbide particle, the nucleation time and temperature, and the LTS time and temperature. Sample calculations and plots are presented. It should be noted that in all equations describing chromium concentration profiles, the parameters of time and temperature always appear together as the product (Dt) of the diffusion coefficient (D) and time (t). This facilitates the use of a simplifying approximation that will be discussed in section 4.0.

3.5 Author: Hattori, S. et al.

Title: Study on Low Temperature Sensitization in Austenitic Stainless Steel Pipe Welds

Reference: Paper No. 6, International LTS Workshop, January 1982

Materials: 304, 304L, 304NG, 316, 316L, 316NG, 347

Carbon: .005-.067%

Test Methods: A262E, A262A

Summary:

This paper supports the general conclusions of the previous papers: commercial grades of 304L and 316L pipes are prone to LTS-enhanced susceptibility to A262E and cold work enhances the likelihood of LTS. The paper also shows that LTS can increase the susceptibility of 304NG and 316NG to A262A. Arrhenius plots are presented that illustrate the effect of strain on the activation energy of LTS. The effect of the temperature at which strain is introduced is also examined. Strain induced at room temperature has a different effect than strain induced at 150°C. Martensite is formed when strain is introduced at room temperature but not at temperatures above 40°C.

3.6 Author: Kawakubo, T., et al.

Title: Effect of Strain on Sensitization of Type 316L Stainless Steel

Reference: Private communication - 1978

Materials: 316L

Carbon: Less than .03%

Test Methods: A262A

Summary:

This paper shows that Type 316L stainless steel (% carbon unknown) can be sensitized and that strain enhances the susceptibility to sensitization. However, an Arrhenius extrapolation of the data obtained at 600°C-500°C predicts that it would require 2,000-5,000 years for sensitization to occur at 300°C.

While Kawakubo's extrapolation was performed correctly, he made an error in calculating the activation energy from the plot. He neglected a factor of 2.3 due to the conversion from base 10 logarithm to base e logarithm. The correct activation energy is 48.3 Kcal/mole instead of 21 Kcal/mole.

3.7 Author: Ljungberg, L.

Title: Low Temperature Sensitization Studies in ASEA-ATOM of Type 304 Stainless Steel

Reference: Paper No. 5, International LTS Workshop January 1981

Materials: 304, 304L

Carbon: .025-.063%

Test Methods: A262E, CERT, TEM, STEM, EPR

Summary:

This paper offers both experimental and theoretical findings. Experimentally, the author concludes that only materials "close to" being sensitized will be affected by LTS. Ljungberg finds that carbides precipitate in 304L, but susceptibility to corrosion does not develop. Ljungberg calculates that it takes 3.4 years for a 200 Angstroms wide chromium depletion zone to develop at 300°C. Several useful exponential temperature curves are presented. There is also a useful comparison between A262E, CERT and EPR.

3.8 Author: Schmidt, C. G., et al.

Title: Low Temperature Sensitization of Type 304 Stainless Steel Weld Heat Affected Zone

Reference: EPRI Project T110-1, Final Report, November, 1983

Materials: 304

Carbon: .068%

Test Methods: EPR, CERT, WOL/CT, TEM, Auger, STEM, EDAX

Summary:

This paper is not a study of low carbon stainless steel, but is of value in that it suggests a mechanism that would offset LTS-enhanced corrosion. Schmidt suggests that the composition of the chromium carbide particle formed below 500°C is only 28% chromium, compared with the 70-95% contained in carbides formed at higher temperatures of 600-800°C. Schmidt fails to detect chromium depletion by EDAX/STEM (section 3.2.2), but detects chromium depletion on fracture surfaces via EDAX/SEM (section 5.3.1). The authors also seem to play down Auger measurements (mentioned in Conclusions, section 3.4) obtained at the Rockwell Science Center on specimens from the same pipe weld that also detected chromium depletion.

It is suggested that the STEM/EDAX beam width used in this study was too wide (250 Angstroms) to make meaningful measurements of chromium depletion. However, the possibility of a reduction in the chromium content of carbides formed at lower temperature is worthy of further attention. Note that an LTS-enhanced susceptibility to corrosion still existed, even in the case where the chromium content of the carbide was only 28%. Schmidt suggests that other mechanisms, such as low temperature solute segregation, may contribute to the increased susceptibility toward corrosion. The report may also be of value in that it compares three experimental methods, CERT, EPR, and WOL/CT, on the same pipe weld material.

3.9 Author: Fujiwara, K., et. al.

Title: Effect of Chemical Composition on the IGSCC Susceptibility of Austenitic Stainless Steels in High Temperature De-ionized Water

Reference: Paper No. 15, Japan Meeting, EPRI-BWR Owners, May 1978, Central Research Laboratory, Kobe Steel, Ltd, Kobe, Japan, May 31, 1978.

Materials: 304, 304L, 304LN, 316, 316LN, 347
Carbon: .011-.075%
Test Methods: Double U-bend, SEM
Summary:

This paper describes an extensive Japanese alternate alloy qualification program. A total of 22 heats of stainless steels are examined. The results show that sensitization can occur in the low carbon stainless steels, but to a lesser extent than in the regular grades of stainless steels. Fujiwara also shows that 200°C is the most aggressive temperature for the double u-bend test. At 200°C, 304L is attacked to nearly the same extent as 304. No attack was ever observed in 316ELN (extra low carbon plus nitrogen), 316ELC plus Nb, and an alloy with 25% Cr, 22% Ni, 2% Mo, and extra low carbon (.02). The paper should provide ideas for alternate materials for canister alloys.

4.0 Discussion and Recommendations

Type 304L stainless steel is susceptible to sensitization and low temperature sensitization (LTS). Cold work can significantly enhance the kinetics of sensitization and LTS. While no comprehensive studies have been performed on the quantitative relationship between cold work and the subsequent rate of LTS, severe cold work has been observed to bring about LTS-enhanced susceptibility to corrosion within the times and temperatures associated with the initial stage of nuclear waste storage. Figures 3 and 4 compare the LTS data of Briant to the times and temperatures expected to be associated with nuclear waste storage. It should be noted that Briant's results are from heat treatments at fixed temperatures and are less severe than the cooling behavior of nuclear waste. Figure 3 shows that the thermal exposure of the outside surface of the canister resulting from the molten glass could cause sensitization before the outside of the canister wall cools. After emplacement in the repository the temperature rises and subsequent slow cooling would continue to increase the degree of sensitization even further. Figure 4 shows that the heat generated by the radioactive decay of the nuclear waste will keep the canister at 280°C for about 10 years. That initial exposure alone is very close to the extrapolated fixed temperature data of Briant and could possibly produce a sensitized microstructure.

Given that the equations for chromium depletion always contain the parameters of time (t) and temperature (T) as the product of the diffusion coefficient (D) and time (t), then some simplifying assumptions and approximations can be made.

As long as the product Dt, is the same (regardless of the exact values of t, T, or D), the chromium concentration profile as a function of distance away from the carbide will be (approximately) the same. Therefore, a heat treatment at temperature T_2 for time t_2 can be equated to a heat treatment at temperature T_1 for time t_1 via:

$$D_1 t_1 = D_2 t_2$$

$$t_1 = t_2 \exp\left\{- \left(\frac{E}{R}\right)\frac{T_1 - T_2}{T_2 T_1}\right\}$$

Assuming that $D_n = D_o \exp\left\{- \frac{E}{RT_n}\right\}$

Using the above equation, the molten glass pour cooling curve from 559°C to 300°C (Figure 1) was broken up into 1-minute steps and an equivalent isothermal heat treatment time at 550°C was calculated to be 38 minutes via the program described in section 7A. The equivalent heat treatment time at 500°C was calculated to be 192 minutes (.133 days) using the second program described in section 7B. These calculations do not account for the lower solubility of chromium carbide at lower temperatures. Hence the actual DOS created by the cooling curve would be more severe than the DOS created by 500°C/192 minutes.

Therefore, the entire molten glass cooling curve can be conservatively approximated by a single data point at 500°C/.133 days. That point is well below Briant's curve for sensitization to occur in cold worked Type 304L stainless steel (Figure 3). Similarly, the long-term thermal exposure from 300°C to 100°C would increase the DOS even further.

Given that the present procedures for the fabrication of nuclear waste canisters do not include a stress-relief or solution anneal after welding, and that abrasive procedures will be used to clean the outside surface of the canisters prior to storage, Type 304L stainless steel would not be the preferred material of construction for nuclear waste storage canisters. Significant improvements in the long-term resistance to sensitization, LTS and corrosion can be achieved with modest changes in alloy composition and fabrication procedures.

While there are a number of corrosion tests, such as A262E and A262A, that can be used to establish a relationship between LTS and subsequent susceptibility to corrosion, the only meaningful corrosion test is one that best simulates the worst, but yet realistic, environmental conditions likely to be encountered in the specific application of interest. For example, in the case of nuclear waste storage canisters, the worst realistic environment likely to be encountered would be some form of ground water concentrated by boiling due to contact with a canister above 100°C. There is also the potential for radiolysis of the water and the chemical species dissolved in the water. The other components for corrosion and stress corrosion also need to be considered. These include stress and material susceptibility. The contact of a hot canister with cool liquid water could cause large thermal stresses and strains in the canister walls. If the outer surface of the canister was cold worked due to abrasive cleaning, then strain above the yield point of the surface layer would produce crack initiation. These crack initiation sites would then form micro crevices, and crevice corrosion could become possible.

With respect to measuring material susceptibility, it is necessary to perform corrosion tests on actual canisters to assure that the same form of material (plate), fabrication stresses (rolled, welded, abrasively cleaned), and thermal history are reproduced. It is recognized that an extensive number of screening tests can be performed on less expensive samples of material, such as rod or bar stock. However, the final qualification testing requires coming as close to the real thing as possible. This is particularly true when testing for susceptibility to LTS. For example, earlier work on stainless steel wires (Povich, 1978) indicated an activation energy for LTS to be 60-70 Kcal/mole and predicted 1,000-2,000 years would be required for LTS to occur at BWR operating temperatures (288°C). However, experiments on samples cut from actual welded pipe indicated an activation energy of 40 Kcal/mole, and LTS within 10-20 years at BWR operating temperatures. Even cutting samples from the canister may alter the residual stress and the results of corrosion tests. In the case of stainless steel piping treated by induction heating to introduce compressive stress on the inside surface of the pipe wall, removal of a specimen from the pipe wall would eliminate the compressive stress, and corrosion tests on such a specimen could erroneously predict a high degree of susceptibility to corrosion. On the other hand, a crevice pipe test on the entire pipe (with compressive stresses intact) would not result in corrosion.

It should also be noted that a thermal gradient through the canister wall (with the inside hot and the outside cool) can put tensile stress on the outside wall of the canister.

5.0 Summary

A review of the literature on low temperature sensitization (LTS) has been conducted to determine if LTS-related microstructural changes can occur in Type 304L stainless steel within the times and temperatures associated with nuclear waste storage. It was found that Type 304L stainless steel is susceptible to sensitization and LTS, and that cold work plays an important role in determining the rate of LTS. Severely cold worked Type 304L stainless steel would clearly develop LTS-related microstructural changes within the times and temperatures associated with nuclear waste storage. These changes could lead to increased susceptibility to corrosion. Significant improvements in the long-term resistance to sensitization, LTS and corrosion can be achieved by modest changes in alloy composition and fabrication practices. Therefore, Type 304L would not be the preferred alloy of construction for nuclear waste storage canisters. The final qualification of an alternate canister alloy should involve corrosion experiments on actual canisters. Suggestions for alternate canister alloys are 316L, 316LN, 316ELC, 347, and XM-19.

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7.0 COMPUTER PROGRAMS

```
 90 REM PROGRAM   "T1*D1=T2*D2"
 100 REM CALC OF TIME AT TEMP K2
 EQUIVALENT TO TIME T1 AT K1.
 102 REM ADDS UP ALL HEAT TRTMTS
 INTO ONE TIME AT TEMP K1.
 200 PRINT "INPUT Z = NO. OF STE
PS"
 210 INPUT Z
 211 CLS
 220 DIM K(Z)
 230 DIM T(Z)
 250 LET M=150/180
 260 LET E=-40000
 270 LET K1=550+273
 280 LET T1=1
 285 LET R=2
 290 LET TIME=T1
 295 LET B=823
 400 FOR N=1 TO Z
 410 LET K(N)=B-M*N
 420 LET T(N)=T1*EXP ((-E/R)*((K
(N)-K1)/(K1*K(N))))
 430 LET TIME=TIME+T(N)
 440 IF N>180 THEN LET M=100/180
 445 IF N>180 THEN LET B=748
 450 NEXT N
 700 LPRINT Z,TIME
 999 STOP
```

```
1                    1.9756695
10                   9.7480867
30                   21.81711
60                   31.329405
120                  37.153662
180                  38.042217
360                  38.394491
```

```
  90 REM PROGRAM NAME = "DECAY"
  92 REM INPUT TIME T1 AT TEMP T
P1AND INPUT TEMP TP2 AND THE TIM
E NEEDED,T2, AT TP2 IS CALCULATE
D.
 100 PRINT "INPUT T1"
 110 INPUT T1
 120 CLS
 130 PRINT "INPUT TEMP 1"
 140 INPUT TP1
 150 CLS
 160 PRINT "INPUT TEMP 2"
 170 INPUT TP2
 180 CLS
 190 LET E=-40000
 200 LET R=2
 300 LET X=TP2-TP1
 310 LET Y=(TP2+273)*(TP1+273)
 320 LET Z=X/Y
 400 LET T2=T1*EXP ((E/R)*Z)
 500 PRINT "T2=";T2
 510 PRINT "T1=";T1
 520 PRINT "TEMP 1=";TP1
 530 PRINT "TEMP 2=";TP2
 540 PRINT "E=";E
 999 STOP


T2=192.62862
T1=40
TEMP 1=550
TEMP 2=500
E=-40000
```

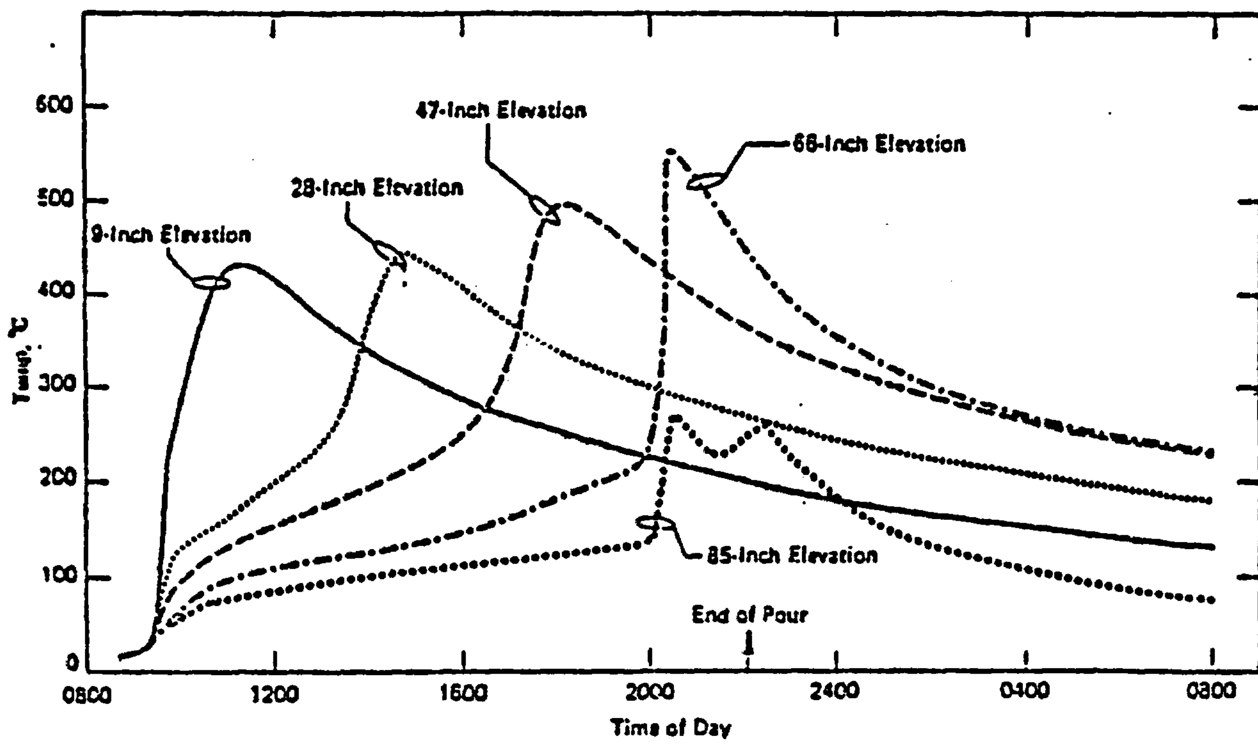

Figure 1: Cooling curves for full-size canisters filled with glass under reference conditions.

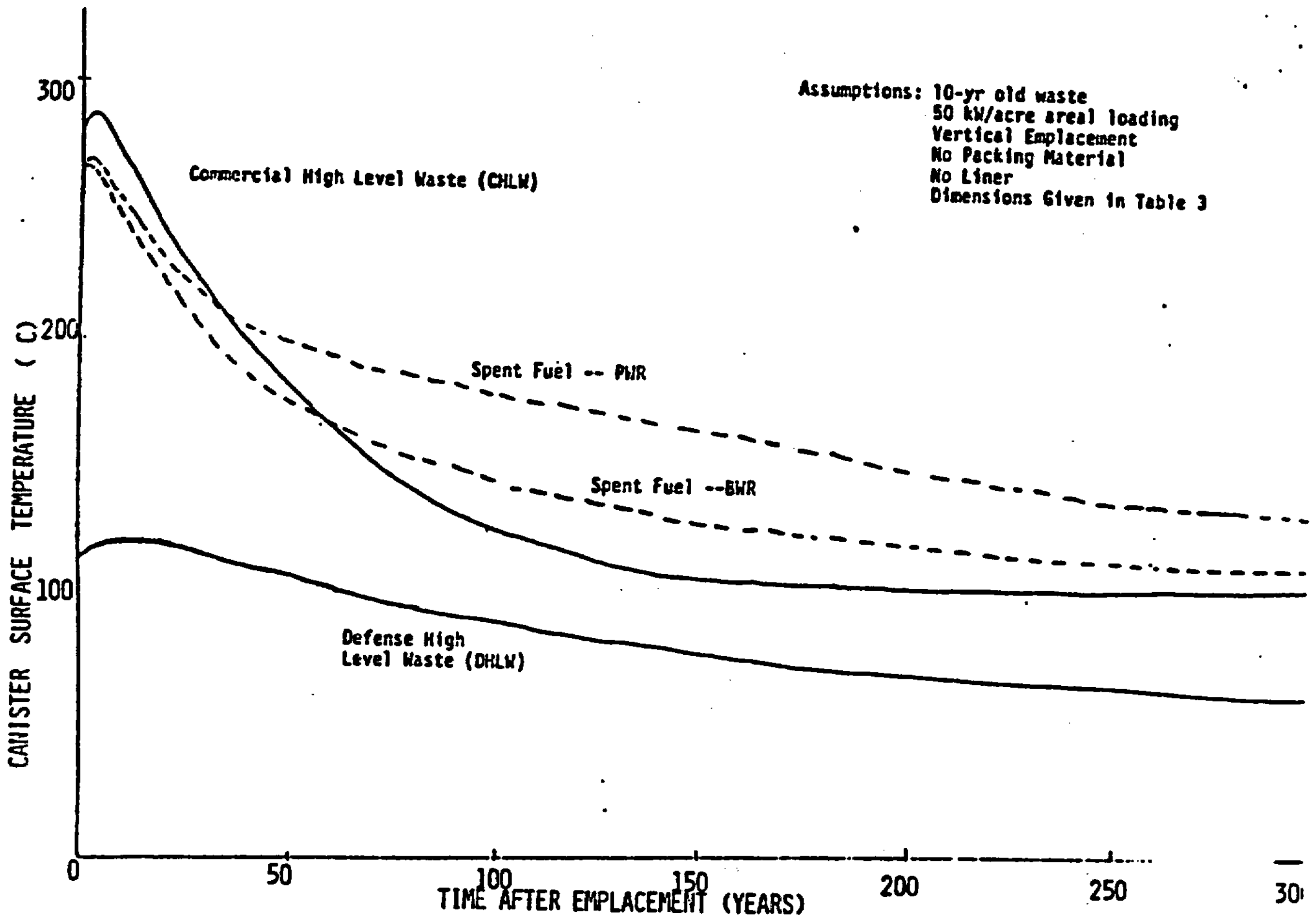

Figure 2: Comparative canister surface temperature-time profiles for different waste packages in a tuff repository.

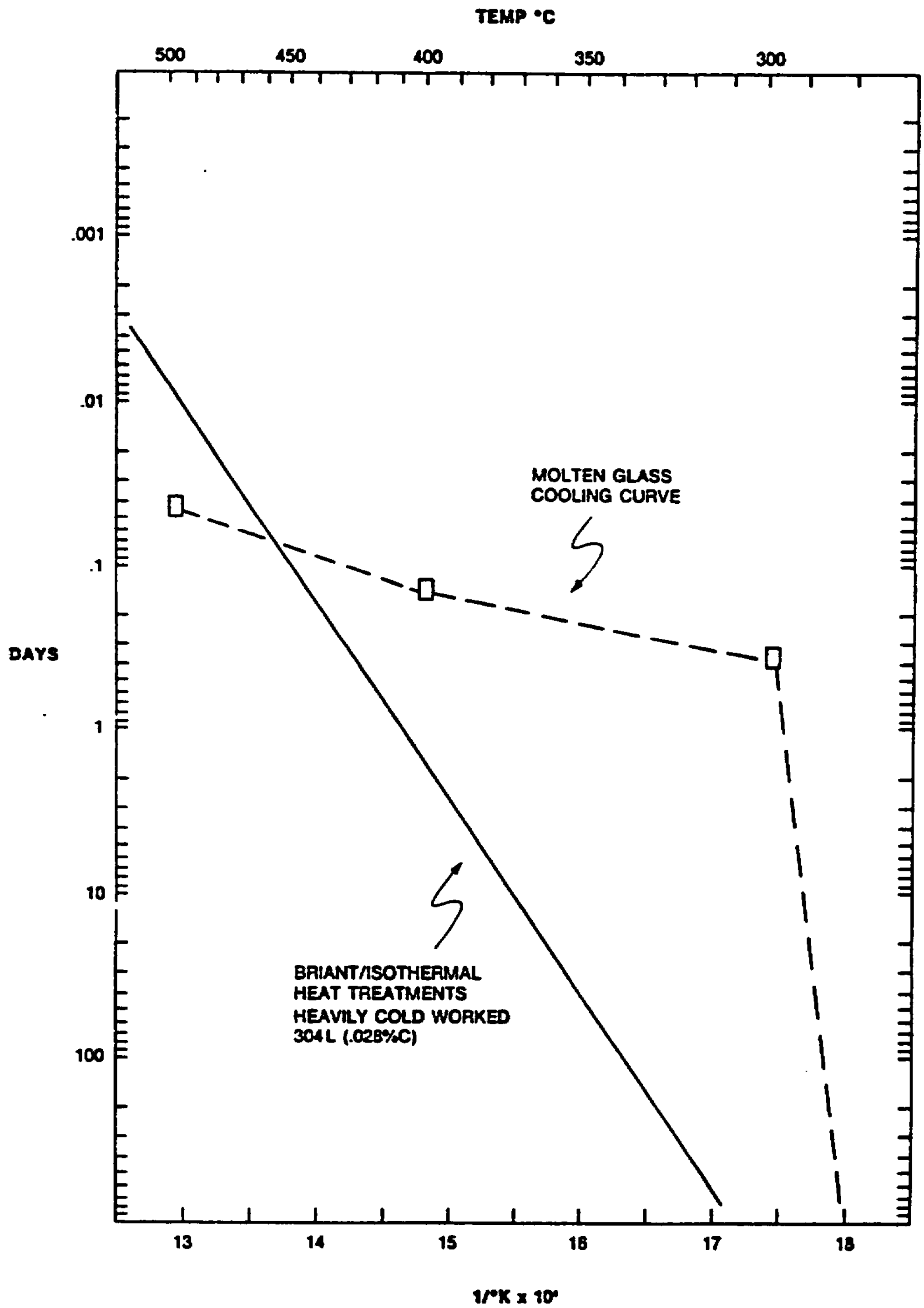

Figure 3: Comparison of Briant's isothermal heat treatment data to the nuclear waste/molten glass cooling data. The three data points from cooling represent the time above that temperature. The combined effect of cooling could be represented as one isothermal heat treatment at 500 C for .133 days.

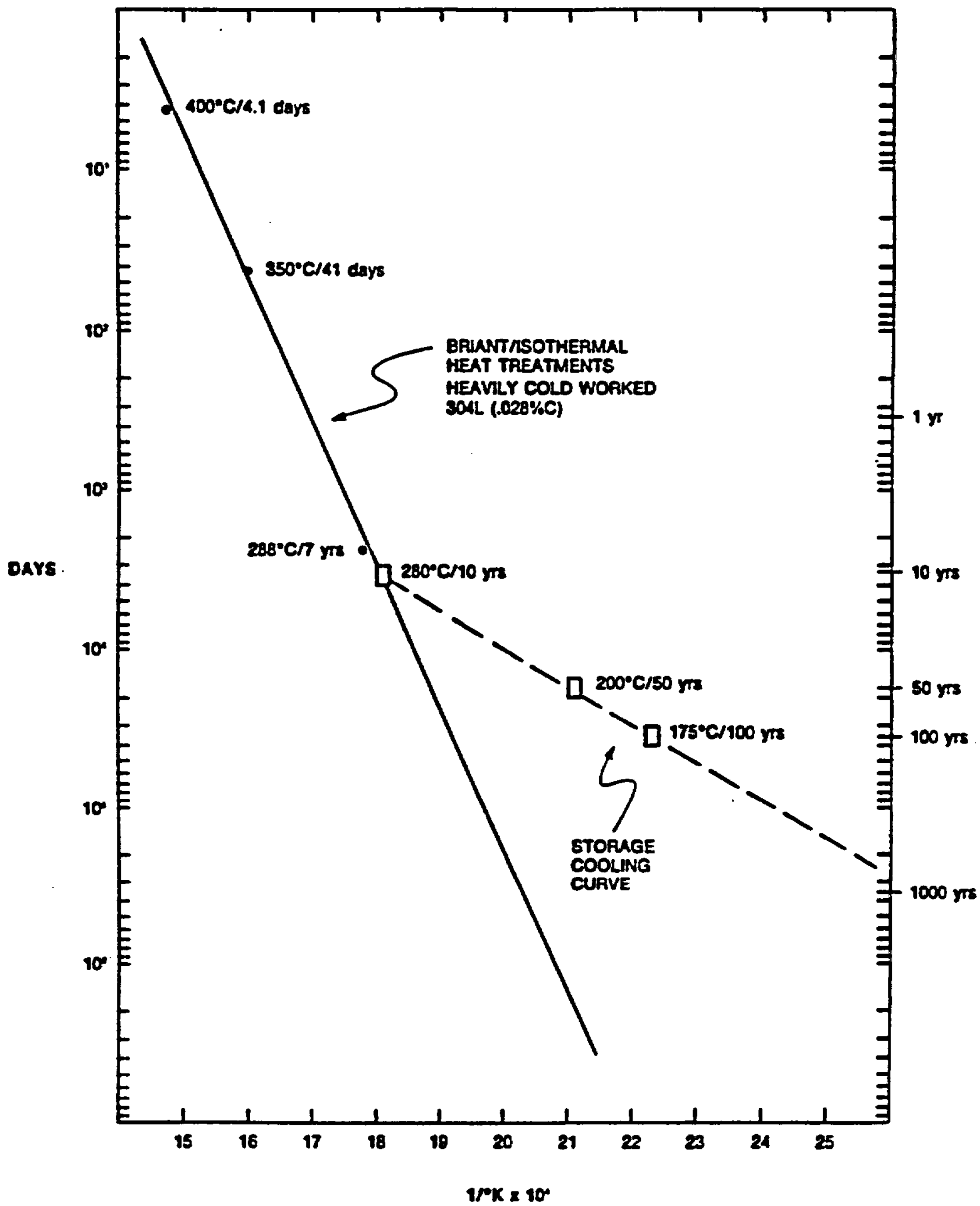

Figure 4: Comparison of Briant's isothermal heat treatment data to the long-term cooling behavior of nuclear waste storage.