APPENDIX B

SELECTION OF MATERIALS

The material for the primary containers in the waste tanks must provide two main functions: it must resist the mechanical forces exerted on the vessel by its contents; and it must resist chemical attack or corrosion by these contents.

Design of the vessels according to the ASME Code, Section VIII, for the construction of pressure vessels and the use of materials approved by that Code ensures that the mechanical requirements are satisfied. This practice has been followed for each successive series of tanks. However, three different specifications of steel have been used to obtain improved performance and reliability as technology improved over the years. These steels are as follows:

- A 285 Grade B — an intermediate-strength carbon steel intended for welded pressure vessels. It may be made by any of the customary steelmaking practices; austenitic grain size is not specified. Toughness is also not specified. This steel is used in Tanks 1 through 16.

- A 516 Grade 70 — a fine-grain-size carbon steel for welded pressure vessels. This grain size may be provided in the normalized heat treatment where improved notch toughness is important. It is used for Tanks 25 through 37. The steel for Tanks 25 through 28 was normalized, but that for Tanks 29 through 34 (actually constructed earlier) was not.

- A 537 Class I — a heat-treated carbon-manganese-silicon steel of fine-grain size for fusion welded pressure vessels. Grade I must be normalized. This steel has very good notch toughness. It is used for Tanks 38 through 51.

The specifications for each of these steels are summarized in Table B-1.

TABLE B-1

Steel Specifications for SRP Waste Tanks

Chemical Composition, %	A-285 Grade B	A-516 Grade 70	A-537 Class I*
Carbon, max	0.22	0.28	0.24
Manganese	0.98 max	0.79-1.30	0.64-1.46
Phosphorus, max	0.035	0.035	0.035
Sulfur, max	0.040	0.040	0.040
Tensile Requirements			
Tensile Strength, ksi	50-70	70-90	70-90
Yield Strength, min. ksi	27	38	50
Elongation in 8 in., %	25	17	18
Nil Ductility Transition Temperature, max °F	**	As rolled** Normalized, -10	-10

* A-537 will contain minor amounts of the following alloying constituents not to exceed

Copper	0.35%
Nickel	0.25%
Chromium	0.25%
Molybdenum	0.08%

** Not specified.

CORROSION

Four distinct forms of corrosion attack may be observed in systems such as the waste tanks.

- General corrosion — the surface is attacked uniformly resulting in a gradual thinning of the structure.
- Pitting — the surface is attacked at very localized sites forming relatively deep pits or crevices. Pitting may cause very rapid penetration of the structure.
- Beachline attack — the metal is attacked more rapidly at the liquid-air (vapor) interface.
- Stress corrosion cracking (SCC) — under the influence of an internally or externally imposed stress and a slightly corrosive environment, the metal cracks at an externally imposed load much lower than its normal tensile strength.

Significant general corrosion has not been observed in the waste tanks as evidenced by the inspection program (both wall thickness measurements and direct observation), as well as by the performance of in-tank corrosion coupons.[1]

Apparent stress corrosion cracking has been observed in six of the nine tanks in which salt deposits have been found in the annular space; SCC is presumed to be responsible for the leaks in the other three. Pitting (and possibly beachline attack) has not appeared to be a problem in the waste tanks themselves, but has caused leaks in about 10% of the cooling coils installed in Types I and II tanks.[2] These corrosion mechanisms have been studied in the laboratory in an effort to select better materials of construction for new tanks and to control operating conditions to prevent additional failures.[1]

Stress Corrosion

Stress corrosion cracking occurs in many metals and alloys. In most of the cases, neither significant corrosion nor stress alone would cause structural failure, but together they can.

Mild steels (a generic name for a class of steels that contains less than about 0.3% carbon) are susceptible to SCC in nitrate solutions as well as in caustic solutions and several other environments.[3] The precise mechanism for this form of failure is not universally agreed upon, but it is no doubt related to the fact that in a crevice or a crack the chemistry of the system can be very different from that in the bulk solution. The most generally accepted mechanism is that the stress maintains a crevice in which the solution is aggressive towards the metal. The chemistry of the solution at the crack tip has been shown to be significantly different from that of the bulk solution by measurements of the pH — an indication of the concentration of hydrogen ions or the relative concentration of acid. Laboratory measurements have shown the pH in the crack tip region to be about 3, acid, while the bulk solution was near neutral, a pH of 7.[4] A solution with a pH of 3 readily corrodes mild steel. A characteristic of this type of cracking is that it is intergranular. That is, the grain boundaries of the metal are preferentially attacked. Intergranular corrosion is the type of attack observed in the SRP waste tank cracking. This evidence, along with electrochemical behavior of the steel, indicates that the cracking in waste tanks has been caused by nitrate stress corrosion.

Waste Composition and Cracking

The waste supernate is basically an alkaline nitrate solution. Although either nitrate or caustic ions can cause mild steel to stress crack, the presence of either will inhibit cracking by the other. Also, nitrite, NO_2^-, is known to inhibit nitrate crack growth,[5] and its concentration in the SRP waste increases with aging. Therefore, the SRP waste solutions contain species that can both cause and inhibit stress corrosion cracking of the mild steel tanks.

Laboratory studies in which specimens are forced to crack by applied tensile loads have led to an understanding of the conditions required for stress corrosion cracks to develop in the waste tanks, and provide a basis for controlling the waste compositions to avoid SCC. During most waste storage operations, technical standards require that the composition of the wastes be controlled as shown in Table B-2. A maximum NO_3^- concentration is specified to limit the maximum aggressiveness of the supernate. The concentration of inhibitors, OH^- and NO_2^-, is maintained at specific minimum levels depending on the NO_3^- concentration. These levels of OH^- and NO_2^- have been shown to prevent crack initiation even in highly stressed specimens.

The temperature of fresh supernate is maintained at less than 70°C. Since stress corrosion is a thermally activated process, this relatively low temperature requirement will also inhibit the initiation and growth of cracks. The temperature limit specifically applies to fresh waste only because aged and evaporated waste contain sufficient OH^- and NO_2^- to inhibit SCC by themselves.

Data from these same laboratory studies confirmed that A 516-70 steel used in Type III waste tanks is less susceptible to cracking than the A 285-B steel used in Types I and II tanks and that the supernates from salt receiver tanks are of the least aggressive compositions, while fresh wastes (high nitrate) are of the most aggressive ones.[6] A 537-I steel has essentially the same corrosion behavior as A 516-70 steel.[7]

TABLE B-2

Required Minimum OH^- and NO_2^- Concentrations in SRP Wastes

Concentration, M		
NO_3^-	OH^-	$OH^- + NO_2^-$
3-5.5	0.3	1.2
1-3	0.1 [NO_3]	0.4 [NO_3]
<1	0.01	—

Residual Stresses and Heat Treatment

Besides a chemically aggressive environment, the other necessary condition for SCC is the presence of tensile stresses in the metal. In large engineering structures, there are generally three types of stresses: (1) working stresses due to the load the structure was designed to carry, (2) reaction stresses — long range stresses due to fabrication, and (3) residual stresses — short range stresses due to fabrication procedures such as welding and deformation to make parts fit together.

Working stresses in such structures have been traditionally designed to be low, about 1/2 or less of the yield stress of the material in accordance with the ASME Boiler and Pressure Vessel Code;[8] this is the case for the SRP waste tanks. Reaction stresses are difficult to estimate quantitatively. However, even though the waste tanks are large, they are simple structures, basically free-standing right-circular vessels, that are built on stable, reinforced concrete pads. Therefore, the reaction stresses in the tanks from such phenomena as settling should be very low.

The tanks are made by welding individual preformed plates together. Since welding involves heating the metal to its melting point with subsequent cooling and solidification, contraction of the metal occurs in a localized, relatively small region. This thermal contraction is nonuniform and leads to built-in stresses that can exceed the yield stress of the material.

Cracks in the waste tanks have been predominantly associated with welds. Cracks form at right angles to the weld bead. They grow a short distance from the weld, then stop. The largest observed crack in a waste tank is six inches long.[9] Cracks stop growing as a result of the rapid decrease of the tensile stress with distance from the weld. These residual welding stresses can be relieved by uniformly heating a structure to a sufficiently high temperature (approximately 1100°F in mild steels) to allow the metal to relax because its strength decreases at elevated temperatures. Such heat treatment eliminates SCC by removing the stress.

FRACTURE TOUGHNESS

Mechanical failure of an engineering structure, such as a waste tank, may be plastic or brittle. Engineering experience and well-understood design criteria have minimized the susceptibility of most structures to plastic failure by overloading. For example, the common engineering practice of fixing the design stress at one-half the yield stress of the material, as in the waste tanks, makes plastic failure improbable. However, brittle fracture at overall stresses less than the yield stress is possible in structures that contain flaws (or so-called "stress raisers"), such as stress corrosion cracks.

Brittle fracture depends on the local conditions in a structure such as the state of stress, flaw size, temperature, and toughness of the material.[10] Brittle fracture may occur by two different modes, ductile or brittle, that reflect differences in the mechanism of fracture on the atomic level. In the case of mild steels, the temperature is very important because the steels exhibit sharp transitions in toughness in a narrow temperature range. At temperatures above the transition the mode of failure would be ductile, and below, brittle. The transition temperature of the steel depends on processing history, chemical composition, and thickness. For example, a normalizing heat treatment of as-rolled plate will lower its transition temperature by at least 30°C. Normalizing consists of heating the steel to 1650°F (about 900°C) and cooling it in air.

Brittle fracture in a ductile mode has been analyzed and requires a flaw 1 to 2 feet long with stresses equal to the yield stress of the steel.[11] The longest known crack in an SRP waste tank is six inches. Since cracks would leak so rapidly before growing to a length of 1 to 2 feet, the waste would have to be transferred to a spare tank before gross failure could occur in this mode.

Brittle fracture in a brittle mode can occur below the transition temperature, and be initiated by relatively small flaws.[12] Therefore, the transition temperature of the steel used in the waste tanks is important.

The toughness of the steel (and thus resistance to brittle fracture) used to build each successive group of tanks has improved concurrently with the evolution of understanding of brittle fracture of large structures. The toughness of the materials as measured by the nil ductility transition temperature (NDTT) is given in Table B-2. Initially, for the Types I and II and early Type III tanks, as-rolled steel was used, and the NDTT was not specified. (In fact, the drop weight test used to measure the NDTT was not developed until 1958-1960, and was not in general use until the mid-1960s.)[13] For these tanks, fracture control is being achieved by ensuring that the steel temperature is above the NDTT by adjusting the temperature of the annulus ventilation air. For the Type III tanks constructed after 1974, normalized steel with specified maximum NDTT will be used. A low enough NDTT is being specified (-10°F maximum, see Table B-1), so that maintaining the minimum tank wall temperature given in Table B-3 will eliminate brittle fracture as a credible failure mechanism.

TABLE B-3

NDTT of Steels Used in Waste Tank Construction

Tank Design	Material, Steel Alloy	Maximum NDTT, °C	Minimum Tank Wall Temperature, °C
Types I and II	A 285-B	20*	20
Type III			
Prior to FY-1974	A 516-70 as-rolled	15**	20
FY-1974	A 516-70 normalized	-18**	15
After FY-1974	A 537 Class I	-45***	10

* Data for A 285-C, see Reference 2.

** Unpublished data from Metal Properties Council.

*** Unpublished data from Lukens Steel Co.

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