100F-8810238--1

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This paper was prepared for submittal to the Materials Research Society Meeting, Berlin, F.R.G., October 10-13, 1988

November 4, 1988

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## LOCALIZED CORROSION AND STRESS CORROSION CRACKING OF CANDIDATE MATERIALS FOR HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL CONTAINERS IN U.S. : A LITERATURE REVIEW

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## ABSTRACT

Three iron-based to nickel-based austenitic alloys and three copper-based alloys are being considered in the United States of America as candidate materials for the fabrication of Ligh-level radioactive waste containers. The austenitic alloys are Types 304L and 316L stainless steels as well as the high-nickel material Alloy 825. The copper-based alloys are CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni). Waste in the forms of spent fuel assemblies from reactors and borosilicate glass will be sent to a proposed repository at Yucca Mountain, Nevada. The decay of radionuclides will result in the generation of substantial heat and in gamma radiation.

Container materials may undergo any of several modes of degradation in this environment, including: undesirable phase transformations due to a lack of phase stability; atmospheric oxidation; general aqueous corrosion; pitting; crevice corrosion; intergranular stress corrosion cracking (IGSCC); and transgranular stress corrosion cracking (TGSCC). This paper is an analysis of data from the literature relevant to the pitting, crevice corrosion, and stress corrosion cracking (SCC) of these alloys.

Though all three austenitic candidates have demonstrated pitting and crevice corrosion in chloride-containing environments, Alloy 825 has the greatest resistance to these forms of localized attack. Both Types 304L and 316L stainless steels are susceptible to SCC in acidic chloride media. In contrast, SCC has not been documented for Alloy 825 under comparable conditions. Gamma irradiation has been found to enhance SCC of Types 304 and 304L stainless steels, but it has no detectable effect on the resistance of Alloy 825 to SCC. Furthermore, while microbiologically induced corrosion effects have been observed for 300se ies stainless steels, nickel-based alloys such as Alloy 825 seem to be immune to such problems.

Of the copper-based alloys, CDA 715 has the best overall resistance to localized attack. Its resistance to pitting is comparable to that of CDA 102 and superior to that of CDA 613; its resistance to crevice corrosion is comparable to that of CDA 613 and superior to that of CDA 102. Observed rates of dealloying in CDA 715 are less than those observed in CDA 613 by orders of magnitude. The resistance of CDA 715 to SCC in tarnishing ammonical environments is comparable to that of CDA 102 and superior to that of CDA 613. Its resistance to SCC in nontarnishing ammonical environments is comparable to that of CDA 613 and superior to that of CDA 102.

# INTRODUCTION

Iron-based and nickel-based austenitic alloys and copper-based alloys are being considered as candidate materials for fabrication of the metal containers to be used in disposing of high-level radioactive waste at the Yucca Mountain site in Nevada. The austenitic alloys are Types 304L and 316L stainless steels and Alloy 825. The copper-based alloys are CDA 102 (oxygen-free Cu), CDA 613 (Cu-7AI), and CDA 715 (Cu-30Ni). These materials are leading candidates because of their good corrosion properties, their wide use in the marine, nuclear, and process industries, and their reasonable cost.

The containers must be retrievable for 50 years and exhibit substantially complete containment for 300-1000 years following repository closure [1, 2]. Shortly after emplacement of the containers in the repository, radicactive decay of the stored waste results in substantial heat generation to the surroundings. For waste packages with the highest thermal outputs, the container surface temperature will rise to a peak temperature of approximately 250°C. After 100 years, the temperature will drop to approximately 150°C and will continue dropping slowly. Containers with lower heat output and those located at the edge of the repository will develop lower temperature peaks.

After emplacement, the container materials could undergo any of several modes of degradation, including atmospheric oxidation, general aqueous corrosion, and various forms of localized corrosion (LC) and SCC. LC phenomena include crevice corrosion and pitting. IGSCC and TGSCC are forms of stress corrosion. In many alloy systems, LC and stress corrosion are interrelated because sites of LC attack become sources of stress corrosion initiation. Gamma irradiation and the introduction of microorganisms into the repository environment can significantly alter the chemical conditions and result in enhanced corrosion attack.

The Metal Barrier Selection and Testing Task of the Nevada Nuclear Waste Storage Investigations project has to select the material adequate for repository conditions from the list of candidates. Selection will be based, in part, on data published in the literature. The relevant literature on LC and SCC of the candidate materials is summarized in this paper.

#### LC AND SCC OF THE AUSTENITIC ALLOYS

Penetration rates at local sites of corrosive attack are far greater threats to container life than rates due to general atmospheric and aqueous corrosion. Consequently, these modes of degradation will probably limit container life. In Ref. 3, Farmer et al. have surveyed the literature (211 articles) on LC and SCC of the three austenitic materials.

First, all austenitic candidates (Types 304L and 316L stainless steels and Alloy 825) have demonstrated pitting and crevice corrosion in chloride-containing environments. However, electrochemical polarization data indicate that Alloy 825 has greater resistance to pitting

Fig. 1. Variation of pitting potential of Type 316 stainless steel with chloride concentration and pH in cellulose bleach solutions at 50°C [Ref. 6]. Increases in chloride concentration and decreases in pH increase pitting susceptibility of austentic alloys.



and crevice corrosion than either Type 304L or 316L stainless steel: Alloy 825 (best) > Type 316L > Type 304L (worst). Resistance to pitting is quantified as the difference between the critical pitting potential,  $E_c$ , and the corrosion potential,  $E_{corr}$ . Large potential differences are indicative of materials having high resistances to pitting. In contrast, large differences between the repassivation potential,  $E_p$ , and the critical pitting potential,  $E_c$ , are indicative of materials having the greatest susceptibility to crevice corrosion. As shown in Figure 1 [6], increases in chloride concentration and decreases in pH decrease the pitting resistance of Type 316 stainless steel. Figures 2 and 3 [7] compare the resistances to pitting of Types 304 and 316 stainless steels and Alloys 825 and 625. Of the candidate alloys, Alloy 825 has the best resistance to pitting. Data for Alloy 625 are included because this alloy can be used as a filler metal in welds of Alloy 825. Though Alloy 625 has good resistance to pitting, its phase stability is uncertain. A duplex structure may be possible.

Stressed austenitic specimens in aqueous environments containing sufficient dissolved chloride and oxygen undergo TGSCC. Combinations of chloride and oxygen concentrations known to induce TGSCC are illustrated in Figure 4 [8]. These data, however, are for alkaline phosphate water. Since the repository will be closer to neutral pH and without phosphate, the data may not be relevant to the repository.

Fig. 2. Pitting potential ( $E_c$ ) and corrosion potential ( $E_{corr}$ ) of candidate materials for (a) fast, and (b) slow scan tests in deaerated substitute ocean water (Ref. 7). Of the austenitic candidates, Alloy 825 has the best resistance to pitting. Alloy 625 is a possible weld filler metal but is expensive and has dubious phase stability.



Furthermore, in acidic chloride media, TGSCC has always been observed in U-bend specimens of Types 304L and 316L stainless steels. TGSCC has not been reported for Alloy 825 under comparable circumstances, however. These results are summarized in Tables I and II [9]. On the basis of their relative susceptibilities to SCC, the austenitic candidates are tentatively ranked as follows: Alloy 825 (best) > Type 316L > Type 304L (worst).

IGSCC of austenitic stainless steels such as Type 304 stainless steel occurs when they are subjected to a sufficiently severe combination of stress, corrosive environment, and sensitization, a term denoting increased susceptibility to attack following a thermal exposure that causes chromium-rich  $M_{23}C_6$  carbides to precipitate at grain boundaries. Chromium carbide precipitation in stainless steels occurs in the temperature range of 500°C to 850°C (930°F to 1560°F), with the rate of precipitation controlled by chromium diffusion. Precipitation results in the formation of a narrow, chromium-depleted zone adjacent to the carbides in which the local chromium concentration is below 12 at.%. Since chromium is the element responsible for the formation of stable passive films in stainless steels, localized depletion of this element results in the establishment of an "active path" into the bulk material. Although  $M_{23}C_6$  particles have been observed in all of the austenitic candidates— Types 304L and 316L stainless steels and Alloy 825—the problem is minimized in Types



Fig. 4. Proposed relationship between chloride and oxygen content of alkaline-phosphate-treated boiler water, and susceptibility to TGSCC of austenitic stain/eas steel exposed to the steam phese with intermittent wetting [Ref. 8]. TGSCC would be expected in Type 304 stainless steel (in the unsensitized state similar to 304L) under repository conditions (1-10 ppm oxygen and 10-100 ppm chloride).



Table I. U-bend specimens after 1 month in 0.8% NaCl and 0.5% CH3COOH at 141°C.					
	Corrosion rate				
Alloy	(mm/yr)		SCC		
304	0.03	Severe pitting	Yes		
304L	0.02	Severe pitting	Yes		
316	0.01	Severe pitting	Yes		
316L	< 0.01	Pitting	Yes <sup>a</sup>		
825	<0.01	No attack	No		

Note: SCC was observed in the 300-series alloys after 30 days of exposure; no SCC was observed in Alloy 825 or the highernickel-content alloys.

One specimen out of two cracked.

Alloy	10-day exposure	30-day exposure		
304	No cracking	Cracking		
304L	No cracking	Cracking		
316	No cracking	Cracking		
316L	No cracking	Cracking		
825	No cracking	No cracking		
Note: All specimens with no cracking after the 10-day exposure were further tested for an additional 20-day exposure. The temperature of the container was maintained at 285°C.				



304L and 316L by low carbon content and is prevented in Alloy 825 by stabilization and the addition of titanium.

Two special circumstances encountered in the repository have been addressed. Figure 5 shows that gamma irradiation enhances IGSCC of Type 304 stainless steel under some conditions [10]. In contrast, Alloy 825 shows no change in its resistance to IGSCC in the presence of gamma irradiation. Though microbiologically induced corrosion and possible SCC have been observed for 300-series stainless steels, the nickel-based alloys such as Alloy 825 seem to be immune to such problems.

From the survey of the literature on crevice corrosion, pitting, and SCC in austenitic steels [3], it is found that Alloy 825 is the candidate most resistant to these forms of localized attack.

### LC OF THE COPPER-BASED ALLOYS

In Ref. 4, Farmer et al. have surveyed the literature (123 articles) on pitting and crevice corrosion of the copper-based alloys. Pitting and crevice corrosion are two of the most common forms of LC of copper-based alloys. Pitting usually occurs in water that contains low concentrations of hydrogen carbonate (bicarbonate) and chloride anions, such as water from well J-13 at the Nevada Test Site. Consequently, this mode of degradation might occur in the repository environment.

The copper-based candidate materials are sensitive to several species that may exist in the repository environment. Ions known to play an important role in pitting include  $S^{2^{\circ}}$ , HS<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2<sup>2</sup></sup>, Cl<sup>-</sup>, Fe<sup>3+</sup>, and H<sup>+</sup>. Dissolved O<sub>2</sub> is also very important. In addition to the reduction of oxygen, the reduction of ferric ion to ferrous ion can serve to depolarize anodic reactions involved in pitting and SCC.

Type 1 pitting is usually associated with certain hard or moderately hard well waters. This type of pitting is believed to be due to a continuous carbon film formed on the inner surface of tubes during bright annealing. It is more likely to occur in cold water than hot water and may cause perforation of tubes after only one year of exposure. It is characterized by the formation of fairly large, well-defined pits, usually containing soft crystalline cuprous oxide, and often cuprous chloride, beneath hard green mounds of calcium carbonate and basic copper carbonate. The surface between the pits is often covered with a shiny, dark red, water-formed cuprous oxide layer beneath a greenish deposit of hardness salts stained with traces of copper corrosion products [11, 12].

Type 2 pitting occurs on hard-drawn tubes in hot tap water of low pH (<7.4) and a low [HCO3]:[SO4] ratio (<1). This type of pitting is practically unknown if the water temperature is below 60°C (140°F). It is characterized by deep pits, of small cross section, containing very hard crystalline cuprous oxide and capped by small black or greenish-black mounds of cuprous oxide and basic copper sulfate [11, 12].

Since J-13 well water has a neutral pH and a [HCO3]:[SO4] ratio much greater than unity, pitting of carbon bearing copper containers in the repository is expected to be Type 1 and would occur only after the surface temperature drops below 60°C, which will require several hundred years.

Crevice corrosion is a form of localized attack that occurs at shielded areas on metal surfaces exposed to certain environments. The sites for this type of corrosion are often unavoidable because of structural or functional design and may even arise during the exposure period. Examples of sites include spot-welded lap joints, threaded or riveted connections, gasket fittings, porous welds, valve seats, coiled or stacked sheet metal, marine or debris deposits, and the water line.

The penetration of corrosive solutions into these relatively inaccessible areas, with widths that are typically a few thousandths of an inch, can result in various types of failures: the metal surface may become stained or perforated by the corrosive; the mechanical strength may be reduced below tolerance limits so that fracture occurs from the applied load or from the wedging action of the corrosion products; operating components may seize; or protective coatings may be disbonded from the metal surface.

Much of the theoretical interpretation of crevice corrosion has been associated with some sort of concentration cell wherein aggressive solute species in water become highly concentrated at the crack tip. This concept is based on the fact that the initiation and propagation of localized attack on metal surfaces are influenced by nonuniformity of the corrosive solution. For example, variations in the concentration of ions or dissolved gases may arise along the same metal surface because of the existence of crevices that are relatively inaccessible to fresh electrolyte compared with freely exposed surfaces. Such environmental conditions cause potential differences and influence electrode kinetics to the extent that an electrochemical cell is established, wherein an oxidation process (that is, corrosion) occurs at the anodic sites, and some reduction process (for example, oxygen reduction) occurs at the cathodic sites.

The selection of materials for service where crevice corrosion is a potential problem involves a comparison of their performance under crevice conditions. However, with the possible exception of data from seawater tests, the lack of standard tests has contributed to erratic and nonreproducible results that thwart attempts at establishing meaningful ratings of materials by a comparison of data from several sources. A ranking by Tuthill and Schillmoller [13] of metals and alloys in terms of crevice corrosion resistance in quiet seawater is given in Table III.

Table III. Relative crevice corrosion resistance of metals and alloys in quiet seawater.				
Metal or alloy	Resistance			
Cu-30Ni-0.5Fe (CDA 715)	Best - very little attack			
Aluminum bronzes (CDA 613)	Best - very little attack			
Alloy 825	Less - significant attack			
Copper (CDA 102)	Less - significant attack			
Type 316 stainless steel	Pit initiation at crevice			
Type 304 stainless steel	Pit initiation at crevice			

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Though few quantitative data on LC were found, qualitative information was used to establish the following tentative ranking: pitting corrosion, CDA 102 (best) = CDA 715 > CDA 613 (worst); local dealloying, CDA 102 (best) > CDA 715 > CDA 613 (worst); crevice corrosion, CDA 715 (best) = CDA 613 > CDA 102 (worst); biofouling, CDA 102 (best) > CDA 715 > CDA 613 (worst). The crevice corrosion susceptibility of CDA 102 makes it a less suitable choice even though it performs well in the categories of pitting corrosion, local dealloying. The cupronickel alloy CDA 715 probably has the best overall resistance to such localized attack.

### SCC OF THE COPPER-BASED ALLOYS

In Ref. 5, Farmer et al. have surveyed the literature (117 articles) and established a tentative ranking of the copper-based alloys on the basis of their susceptibility to SCC. The copper-based alloys are susceptible to SCC in moist ammonia-containing environments as well as in nitrite solutions, cupric acetate solutions, and steam. One scenario for the generation of SCC-promoting chemical species on the surfaces of the nuclear waste containers is gamma radiolysis. For example, acidic nitrite could be generated in this manner; thus, radiation-induced SCC may be possible. Figure 6 [14] shows the dependence of the failure stress on nitrite concentration. The specimen was strained at 2.6 x  $10^{-6}$  s<sup>-1</sup> while being maintained at 25°C and 100 mV, SCE. The generation of ammonia by radiolysis is unlikely, though a mechanism has been proposed in the literature for the cathodic reduction of nitrite to ammonia. This proposed mechanism was abandoned by the authors in subsequent publications. If ammonia did form, it would be oxidized by hydrogen peroxide. Hydrogen peroxide is expected to be generated in moisture films but will undergo rapid catalytic decomposition on copper surfaces. There is also a possibility of biological activity in the repository. In such an event, microbes could generate a moist ammoniacal environment having nearly neutral pH. As illustrated in the Pourbaix (potential-pH) diagram for the



Fig. 6. Stress-elongation curves obtained from slow strain rate tests of oxygenfree copper in aerated solutions of NaNO<sub>2</sub> at the concentrations shown: room temperature and an electrode potential of +100 mV (SCE); strain rate =  $2.6 \times 10^{-6} \text{ s}^{-1}$  [Ref. 14]. Nitrite ion can be formed during radiolysis and can promote SCC of CDA 102.

NH<sub>3</sub>-H<sub>2</sub>O-Cu system shown in Figure 7 [15], a singularity exists at a pH of approximately 7.3 and a potential of approximately 275 mV, SCE. The passive film at the tip of SCC cracks is metastable under these conditions. Consequently, such environments promote SCC propagation. Fortunately, as shown in Figure 8 [16], the compositions of CDA 613 (Cu-7Al) and CDA 715 (Cu-30Ni) have been optimized to minimize the susceptibility to SCC in moist ammoniacal environments.

More specifically, IGSCC of copper (CDA 102) is observed in nontarnishing ammoniacal solutions and cupric acetate solutions. TGSCC of CDA 102 is observed in tarnishing ammoniacal and ammonium hydroxide solutions and nitrite solutions. Both film rupture [17] and film-induced cleavage [18] have been used to explain SCC of pure copper and alpha brasses. The tarnish film involved in the SCC of copper is probably Cu<sub>2</sub>O. Growth of this oxide obeys the parabolic law, which is consistent with the film-rupture model as well as the slip dissolution-repassivation model [19]. Copper deoxidized with phosphorus (CDA 122) is prone to both embrittlement and IGSCC. Copper-phosphorus alloys are most susceptible to IGSCC at approximately 0.2 percent phosphorus content [20, 21].

TGSCC of aluminum bronze (similar to CDA 613) is known to occur in moist ammonia-containing environments. Aluminum bronze having aluminum contents intermediate to those of CDA 102 and CDA 613 (approximately 1 percent aluminum) is more susceptible to SCC than aluminum bronze of other compositions [20, 21]. IGSCC of aluminum bronze is known to occur in steam environments, probably because of the formation of Al<sub>2</sub>O<sub>3</sub> at grain boundaries, but it can be effectively inhibited by small additions of tin [21]. The tin impedes the oxidation of intergranular aluminum. Aluminum bronze



Fig. 7. Detailed representations of the regions of singularity that occur on the potential/pH diagram (a) around pH 7.3, and (b) around pH 11.3 [Ref. 15]. Microbial growth can result in moist ammoniacal environments of pH of about 7.3. Such environments are known to promote SCC in CDA 102 (as well as in the other copper-based alloys).





(CDA 613) is very susceptible to dealuminification, which could conceivably induce failure by a film-induced cleavage SCC mechanism. Chloride and sulfate may promote dealloying of materials such as CDA 613; however, these ionic species do not appear to promote SCC directly. This behavior is in contrast to that of the austenitic candidate alloys.

IGSCC of cupronickel alloys such as Cu-30Ni (CDA 715) may occur in steam environments, but these alloys are much less susceptible to IGSCC than aluminum bronzes (without tin inhibitor). TGSCC of cupronickel alloys may occur in moist ammonia-containing environments, but these alloys are much less susceptible to TGSCC than aluminum bronzes (CDA 613). The passive films on cupronickel alloys probably consist of Ni(OH)<sub>2</sub>. Auger spectroscopy has shown that these films primarily contain nickel and oxygen (note that hydrogen cannot be detected by Auger spectroscopy). Similar films would be expected at the crack tip. Though some dealloying may occur in cupronickel alloys (CDA 715), the rates of dealloying are several orders of magnitude smaller than those observed in aluminum bronzes (CDA 613) [22]. Therefore, TGSCC by the postulated mechanism of film-induced cleavage in dealloyed layers would be expected to be a more significant problem in CDA 613 than in CDA 715, though relatively few data exist supporting such TGSCC failures in either material.

The only data found in the literature that allow a direct comparison of the SCC susceptibilities of the copper-based candidate alloys were published by Pugh et al. [20]. These data are not specifically for CDA 613 and CDA 715 but for alloys having close compositions, i.e., Cu-25Ni and Cu-6Al. Furthermore, these data are only applicable to moist ammoniacontaining environments. The data are summarized in Table IV. The following tentative ranking can be inferred for susceptibility to SCC in tarnishing ammoniacal solutions: CDA 715 = CDA 102 (best) > CDA 613 (worst). Correlations between corrosion potential and SCC susceptibility have been established for neutral Mattsson solution which also suggest

Table IV.	Time-to-failure of ammoniacal solutions.				
Solution	Cu	Cu-6Al	Cu-25Ni		
Tarnishing	100,000	2,600	100,000		
Nontarnishing	4,600	16,700	11,900		
Note: Time in seconds; specimens stressed at 10% proof stress.					

that CDA 715 is superior to CDA 613. This ranking is in contrast to the ranking for nontarnishing ammoniacal solutions: CDA 715 = CDA 613 (best) > CDA 102 (worst).

It may be possible for SCC to originate in dealloyed layers and propagate by a film-induced cleavage mechanism. In such cases, SCC susceptibility should be related to dealloying kinetics. On the basis of literature data for dealloying in chloride and sulfate environments, the following ranking can be deduced: CDA 715 (better) > CDA 613 (worse). Obviously, CDA 102 would not fail by this type of mechanism.

On the basis of the limited data available, it can be argued that CDA 715 has the best overall resistance to SCC. However, there is a clear need for additional experimental data. Sufficient quantitative data do not exist for the unambiguous ranking of these materials under conditions that may be more relevant to the repository environment, such as exposure to steam and nitrite.

## CONCLUSIONS AND OUTLINE OF FUTURE WORK

On the basis of this survey on LC and SCC, the candidates are tentatively ranked. Alloy 825 and CDA 715 are believed to have the best overall resistance to these modes of degradation. Though pitting and crevice corrosion may be encountered with all of the candidates, Alloy 825 and CDA 715 seem the least susceptible to these forms of attack. Under environmental conditions known to induce SCC of Types 304L and 316L stainless steels, Alloy 825 appears resistant to this mode of degradation. Similarly, CDA 715 is the cnly copper-based alloy that appears to have good resistance to SCC over a broad range of conditions known to cause failure in CDA 102 and 613.

We have tried to bracket the available information around the physical, chemical, metallurgical, and mechanical conditions that are expected to occur during the containment period at Yucca Mountain. However, it is important to note that these rankings are based on information in the general technical literature, and while the literature includes a broad range of environmental conditions, the rankings are not based on experimental work specific to Yucca Mountain.

There are important gaps between conditions described in the literature and the conditions at Yucca Mountain. For instance, the combined effect of a moderately high temperature, high radiation field, and ambient oxidizing conditions on the metal oxidation and corrosion rates is not known. The analysis of information from the survey of degradation modes [3-5] indicates that this lack of correspondence is particularly important in the copper-based materials but less important in the austenitic materials. Much of the data on LC of the copper-based materials appears to be more empirically oriented than otherwise comparable data on the austenitic materials. In the austenitic materials, a higher degree of correlation exists between experimental and field data on the one hand and mechanistic models for predicting behavior on the other.

Although a tentative ranking of the candidate alloys is possible between members of the same alloy family (because alloy composition is often used as an experimental parameter), comparison between candidates in the two alloy families has not yet been made. This comparison is needed as part of the selection process because the plan of the Metal Barrier Selection and Testing Task is to nominate one of the six candidates for future design evaluation. In the next several months, we plan to (1) perform electrochemical determinations of critical LC potentials and incubation times for all of the candidate materials, and (2) generate data on the detection of stress corrosion initiation and progragation in all of the candidate materials, including weldments. The welding processes that we will study are representative of those under consideration for making the closure weld of the containers. Completion of this activity will allow a direct comparison of the behavior of the candidates. Test

environments will be relevant to the repository, although specific aspects of the chemical environment will be modified in order to accelerate degradation so that data can be obtained in a reasonable amount of time.

## ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-74J5-Eng-48. The authors thank Jay C. Cherniak for his editorial assistance and Dennis L. Fleming for typesetting this paper.

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