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Effects of Fluoride and Other Halogen Ions on the External Stress Corrosion Cracking of Type 304 Austenitic Stainless Steel

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ABSTRACT

The drip procedure from the "Standard Test Method for Evaluating the Influence of Thermal Insulation on External Stress Corrosion Cracking Tendency of Austenitic Stainless Steel" (ASTM C 692-95a) was used to research the effect of halogens and inhibitors on the External Stress Corrosion Cracking (ESCC) of Type 304 stainless steel as it applies to Nuclear Regulatory Commission Regulatory Guide 1.36, "Nonmetallic Thermal Insulation for Austenitic Stainless Steel." The solutions used in this research were prepared using pure chemical reagents to simulate the halogens and inhibitors found in insulation extraction solutions.

The results indicated that sodium silicate compounds that were higher in sodium were more effective for preventing chloride-induced ESCC in type 304 austenitic stainless steel. Potassium silicate (all-silicate inhibitor) was not as effective as sodium silicate. Limited testing with sodium hydroxide (all-sodium inhibitor) indicated that it may be effective as an inhibitor.

Fluoride, bromide, and iodide caused minimal ESCC which could be effectively inhibited by sodium silicate . The addition of fluoride to the chloride / sodium silicate systems at the threshold of ESCC appeared to have no synergistic effect on ESCC. The mass ratio of sodium + silicate (mg/kg) to chloride (mg/kg) at the lower end of the NRC RG 1.36 Acceptability Curve was not sufficient to prevent ESCC using the methods of this research.

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INTRODUCTION

The purpose of this research was to provide to the Nuclear Regulatory Commission new information on the effect of chloride, fluoride, bromide, and iodide on ESCC of type 304 austenitic stainless steel, and to determine the role of sodium + silicate as an effective inhibitor for ESCC induced by these ions. The drip test methodology of ASTM C 692-95a (Standard Test Method for Evaluating the Influence of Thermal Insulations on External Stress Corrosion Cracking Tendency of Austenitic Stainless Steel) was used for this study. The topics addressed included : 1) the effect of the molar ratio of sodium-to-silicate in the inhibitor; 2) the amount of sodium + silicate necessary to inhibit the ESCC action for specific amounts of chloride (mass ratio); 3) the presence or absence of a synergistic effect of fluoride on the action of chloride; 4) the possibility for ESCC induced by fluoride, bromide, and iodide ions, and if found, its inhibition by sodium + silicate.

BACKGROUND

External Stress Corrosion Cracking

ESCC is a type of corrosion involving cracking that occurs on the outside surface of thermally-insulated pipes or vessels and is often associated with austenitic stainless steels. For ESCC to take place several factors are usually present: tensile stress, moisture, heat, an aggressive chemical environment, and sensitized metal. Heat-treatment or welding sensitizes the metal by depleting the chromium in the grains and forming chromium compounds at the grain boundaries.

ESCC of insulated pipes became recognized as a serious problem in the 1950's[1], and researchers in the industry quickly devised methods for pre-qualifying insulating materials for use in contact with austenitic stainless steel. Several specifications were promulgated in the sixties and seventies but only two remain: ASTM C 795 (Standard Specification for Thermal Insulation for Use in Contact with Austenitic Stainless Steel) and MIL-I-24244 (Insulation Material, with Special Corrosion, Chloride, and Fluoride Requirements).

Regulatory Guide 1.36 (Nonmetallic Thermal Insulation for Austenitic Stainless Steel) was issued in 1973 and, while not a specification or a regulation, RG 1.36 suggests the use of the ASTM and / or RDT test procedures to qualify insulation for use in nuclear facilities. The ASTM and MIL-I specifications have been periodically updated. The RDT procedures are outdated and have been abandoned (see 3rd paragraph under "History..."). The Nuclear Regulatory Commission, in their efforts to revise RG 1.36, required additional information as noted in items 1 - 4 of the Introduction.

History of ESCC Test Procedures

In the early 1950s, the test method that has become known as the Dana test originated in the DuPont laboratories. It employs electrically-heated 2in.x 7in. (51mm x 178mm) type 304 stainless steel coupons for testing wickable insulations[2]. The metal used in the test must be qualified to establish its propensity for cracking prior to use in the test method. After forming the specimen into a U shape, the specimen is subjected to a quantified post-stressing. This procedure was adopted by ASTM as C 692 in 1971.

The C 692 test method was revised in 1990 to allow for the use of a steam-heated pipe as an alternative to electrical resistance heating. Instead of wicking distilled or deionized (DI) water up to the test coupon, the C 692-90 (drip method) turns the apparatus "upside down" and allows the water to leach downward either through or around the insulation test piece. This method enables the testing of wickable materials as well as those that do not wick. The most recent issue is C 692-95a.

The MIL-I-24244 procedure was developed by the Knolls Atomic Power Laboratory of General Electric[3]. It employs a 1/4in. x 3 1/2in. (6.4mm x 89mm) coupon bent over a steam-heated pipe. Neither qualification of the metal nor post-stressing of the bent coupon is a requirement. The most recent issue was MIL-I-24244C (1987) with Amendment 1 (1990) - allowing the use of ASTM C 692; and Interim Change 1 (1991) - allowing the use of ASTM C 871 (Standard Test Methods for Chemical Analysis of Thermal Insulation Materials for Leachable Chloride, Fluoride, Silicate, and Sodium Ions). The MIL-I-24244 and the RDT M 12-1T test procedures are essentially the same with the MIL-I preceding the RDT standard. RDT M 12-1T was first issued in 1969 and abandoned in 1980.

Stainless Steels

Series 300 stainless steels with low carbon (0.03% or less in types 304L and 316L for example), generally are not subject to ESCC. For ESCC to take place in type 304 stainless steel using C 692 test conditions, several factors must be present: high carbon content, sensitization, tensile stress, moisture, heat, and an aggressive chemical environment. Commercial type 304 stainless steel with 0.05-0.06% carbon usually passes the qualification test as required by ASTM C 692. This metal qualification test requires that four out of four test coupons exposed to water containing 1500 mg/l chloride must crack in three days, and that no cracking occurs on four coupons exposed to deionized water for 28-days.

Corrodants and Inhibitors

It is generally accepted that chloride from insulation or other environmental sources can induce ESCC when in contact with austenitic stainless steel. The deleterious action of chloride ions has been shown to be offset by the presence of suitable amounts of sodium silicate[4] compound.

Fluoride has been "suspect" and, along with chloride, was included in RG 1.36. Fluoride was added to MIL-I-24244 in 1984. An effort to incorporate fluoride into ASTM C 795 (Standard Specification for Thermal Insulation for Use in Contact with Austenitic Stainless Steel) in the mid 1980's failed because no direct evidence could be provided to demonstrate that it was a problem. The other halide ions, bromide and iodide, might be considered "suspect" as well because they are chemically similar to chloride. The results of this study will attempt to resolve these issues.

While the above specifications and guides are used to test for only chloride, fluoride, sodium, and silicate, it is possible that other ions in addition to halides and silicates may contribute to either corrosion or inhibition.

Acceptance Criteria

An acceptability curve based on the water-leachable chemical content of insulating materials has been developed and used in all of the North American guides and test specifications. This curve, shown in Figure 1 (as taken from RG 1.36), relates the amount of "sodium + silicate" to the amount of "chloride + fluoride." As a GUIDE, the acceptability curve indicates that insulation is probably acceptable if the amount of chloride + fluoride vs. sodium + silicate lies below the curve. The primary requirement is that the insulation material must pass a 28-day preproduction corrosion test such as stated in ASTM C 692 or MIL-I-24244.

The source of the acceptability curve was from a paper presented by Karnes[3] in 1965 (Figure 2). The data presented were limited and related only "chloride to sodium + silicate compound." The curve was incorporated into RG 1.36 in 1973 and has been used ever since. Fluoride was incorporated in RG 1.36 presumably because the writers considered that fluoride, another halide sometimes found in insulations, might also contribute to ESCC.

The important point about the acceptability curve is the indication that there should be some significant gravimetric excess of sodium + silicate relative to chloride + fluoride. At the lower end of the curve, the ratio of sodium + silicate to chloride + fluoride is about 3:1, while at the upper end it is about 15:1. Further, the ratio between sodium and silicate is completely undefined, even though the presumption is that some form of sodium silicate compound is present to attain inhibition.

TEST PROCEDURES

ASTM C 692-95a

The testing procedures were based on the test methods of the drip procedure of ASTM C 692-95a. This test method utilizes stainless steel U-bend coupons that are post-stressed and positioned upright on a 1½ inch pipe, steam heated to 212°F (100°C). Insulation is tested by fitting samples to the U-bend coupons and dripping deionized (DI) water onto the insulation. A peristaltic pump delivers 250 +/- 25 ml/day to each test specimen for 28 days.

The stainless steel used in the test must be qualified by using a 1500 ppm chloride solution dripped onto a 1 ½ inch (38 mm) by 3 inch (76 mm) piece of chloride-free Kimwipe tissue paper in place of the insulation . Qualification of the metal requires that 4 out of 4 tested coupons must develop ESCC after 3-days. In addition, a 28-day test using DI water dripped onto the coupons must have no cracks on 4 out of 4 coupons to verify that the metal is not overly sensitive and that the water used is not contaminated.

The research described in this paper substituted various concentrations of simulated insulation extraction solutions in place of the 1500 ppm chloride qualification solution and continued the tests for 28 days or longer. A full description of the solutions used for the tests is provided further in this report.

The metal used was type 304 solution-annealed stainless steel, complying with ASTM specification A 240 and having a carbon content of 0.0545%. The 453 coupons reported on in this paper were cut from a single lot of this metal and all were sensitized in air at 649°C (1200°F) for three hours. The metal lot was qualified by 3-day exposure to a 1500 mg/kg chloride solution at 250 ml/day and resulted in 4 out of 4 coupons having ESCC cracking. A 28-day test with deionized water resulted in no cracks on the 4 coupons tested.

Metal Certification Data

1: Grade and Specifications - Allegheny Stainless Steel Type 304 Sheet C R Coils annealed 2B Fin 3 Edge - -ASTM-A-240-94, Solution-Annealed at 1900F.

2: Physical Properties

Heat	Coil	Test	Yield Str.	Tensile Str.	%Elong(in 2")
868174	06285N551B	7619231	46900 psi*	97500 psi	53

*Y.S. by 0.2% Offset Method

3: Chemical Analysis (%)

C	Mn	P	S	Si	Cr	Ni	Mo	Cu	N
0.0545	1.84	0.031	0.0004	0.43	18.26	8.17	0.45	0.41	0.06

TEST PROGRAM

This research program considered both the effect of different mole ratios of sodium-to-silicate and the effect of the amount of sodium + silicate compound to the amount of chloride (mass ratio). In order to minimize the number of tests in the inhibitor program, only duplicate rather than four coupons initially were tested at each chloride-to-sodium+silicate level. The primary purpose of the inhibitor program was to find the highest chloride level for a given amount and ratio of sodium+ silicate that failed to produce cracks (threshold-chloride pass). When the threshold-chloride pass condition was indicated by both coupons being crack free, the solution concentration was retested and verified with two additional coupons.

The effect of fluoride, bromide and iodide ions on ESCC was investigated using various concentrations, combinations and exposure times. After ESCC was established, the inhibition effect of sodium + silicate was studied. A possible synergistic effect on ESCC from fluoride in combination with chloride was investigated by adding fluoride to the threshold-pass conditions using two different mole ratios of the sodium silicate compound as inhibitors.

Test Solutions

All of the solution concentrations in this report are written as milligrams per liter (mg/l), which is equivalent to parts per million (ppm) as used in existing documents and acceptability curves. Ion concentrations in solid material are written as mg/kg (instead of ppm), to be consistent.

Simulated extraction solutions were made equivalent to the water-leachable ion concentrations found in insulation when analyzed by the methods of ASTM C 871 (Standard Test Method for Chemical Analysis of Thermal Insulation Materials for Leachable Chloride, Fluoride, Silicate, and Sodium). The relationship between the ion content of an insulation sample, the concentration in the simulated extraction solution, and the total amount delivered over the 28-day test period, is shown graphically in Fig 3. For example, an insulation with an ion concentration of 36 mg/kg produced an extraction solution containing 1.42 mg/l of that ion using ASTM C 871 leaching methods. This test condition delivered 10 mg over the 28-day test period using 250 ml/day of a 1.42 mg/l dripped solution. The reported number was 36 mg/kg rather than the 10 mg delivered or the 1.42 mg/l in solution, thus the results directly compare with Karnes' data and previous reports and specifications dealing with insulation and ESCC.

The test solutions to be used on the coupons were made by diluting weighed amounts of concentrated solutions to a specific volume. The concentrated halide solutions were made from chemically-pure (CP), analyzed reagent-grade materials. Concentrated sodium silicate solutions were made from commercial sodium silicate compounds provided by P.Q. Corporation. These solutions were analyzed using the test methods of ASTM C 871 to determine the exact amounts and ratios of silicate and sodium present.

Tables 1 and 2 (Appendix 1) detail the results of the analysis and how the solutions were made. Small quantities of each prepared concentrate were saved for reference. The ratio (in percentages) of sodium and silicate found by chemical analysis for the three sodium silicate compounds used were as follows:

1. SODIUM ORTHOSILICATE	Na (58.7%)	SiO_3 (41.3%)
2. SODIUM METASILICATE	Na (38%)	SiO_3 (62%)
3. SODIUM DISILICATE	Na (22.6%)	SiO_3 (77.4%)

Testing with the "all silicate" inhibitor began with amorphous colloidal silica. A chemical analysis of the material showed that only trace quantities of soluble silicate were present (i.e. the bulk of the material was presumed to have been non-ionized SiO_2). In insulation, such amorphous silica may or may not provide inhibition, depending on the overall composition and the process history of the insulation material after the addition of the amorphous silica. The first test series indicated that the as-received amorphous silica provided little or no inhibiting effect as there were many large cracks on the coupons. All subsequent test series used potassium silicate compound as the "all silicate" inhibitor. Potassium silicate compound was chosen because all of the applicable test methods or specifications measure only sodium, ignoring potassium in the inhibitor chemical analysis. Sodium hydroxide solutions were made from CP NaOH and analyzed for sodium content.

The chloride-to-sodium + silicate inhibitor program first used sodium chloride as the chloride source. Switching to potassium chloride avoided the complication of including sodium from the halide source in the total sodium. All of the early tests with sodium chloride resulted in failures so the "extra" sodium from the sodium chloride was not a factor. The halide ion sources for the other halide tests were potassium fluoride, potassium bromide, and potassium iodide.

Evaluation

Passing the 28-day corrosion test requires that none of the four tested coupons can have any cracks. In severe cases of ESCC, the cracking is evident when the coupon is removed and cleaned. It is often the case that only small spots of discoloration from corrosion products can be seen on the coupon. The current test procedure is to manually flatten the U-shaped coupon and rebend it to roughly the original shape. This aids significantly in cleaning the coupon by loosening any surface accumulation and helps to open the cracks so they can be seen. If cracks are not established, then a dye-penetrant inspection is used to provide guidance as to where to rebend again in the search for cracks. If present, these cracks can be seen with 10x to 30x magnification. As best as can be determined from Karnes' paper the U-shaped test coupons were not straightened and re-bent as a means of inspecting for cracks, and as a result many small, tight cracks may have gone unnoticed.

Only a pass/fail evaluation was used in this program. There were no stipulations for the number of cracked coupons, the number or severity of cracks on the coupon, or the size of the cracks. Many of the failed coupons in this test program exhibited only slight cracks that could be seen only by careful scrutiny with 30x magnification. When "pits" were seen without observable cracks, they were not counted as failures.

RESULTS

Metal Qualification With Deionized (DI) Water

To demonstrate that the stainless steel coupons used in the program were completely unaffected by the DI water being used, two "blank" coupons were run for 84 days. No cracks could be observed. An additional two "blank" coupons were run for 28 days to verify and comply with the 28-day qualification test with deionized water (no cracks on four tested coupons). This qualification test is being incorporated into ASTM C 692.

Inhibitor Program (Identifying the Threshold-Chloride Pass)

The quantity ratios of chloride-to-sodium + silicate for the 28-day tests were chosen to identify the threshold-pass conditions for each sodium silicate compound tested. It was necessary to establish these threshold values of chloride-to-sodium + silicate so that they could be used in the tests designed to determine if fluoride had a synergistic effect on the action of chloride. The threshold-pass condition was indicated when the first two coupons passed the 28-day test. The chloride-to-sodium + silicate condition was checked with an additional two coupons during the fluoride addition tests to establish and verify that the combination of chloride with sodium+silicate would pass. Several of these verification tests resulted in failures indicating that the quantity of inhibitor for that level of chloride was marginal.

The results for the three tested sodium-to-silicate ratios are presented in Appendix A, Tables 3 thru 5 and Appendix B, Figures 4 thru 6 as listed below. The results for the potassium silicate compound tests (all-silicate) are presented in Table 6 and Figure 7. The results for the sodium hydroxide tests (all-sodium) are presented in Table 7 and Figure 11. The threshold-passing conditions identified for the silicates are presented in Figure 8. The acceptability curve (Figure 1) from Karnes' data is shown on each Figure for reference.

Table 3 and Figure 4: -- Na, 58.7%; SiO_3, 41.3% (Sodium Orthosilicate)
Table 4 and Figure 5: -- Na, 38%; SiO_3, 62% (Sodium Metasilicate)
Table 5 and Figure 6: -- Na, 22.6%; SiO_3, 77.4% (Sodium Disilicate)
Table 6 and Figure 7: -- SiO_3, 100% (Potassium Silicate)
Table 7 and Figure 11: -- Na, 100% (Sodium Hydroxide)
Figure 8: -- Verified threshold passes for different $Na:SiO_3$ ratios

Synergistic Effect of Fluoride on the Action of Chloride

Tests were run adding fluoride to several threshold-passing chloride with sodium orthosilicate and sodium metasilicate inhibitor combinations to determine if fluoride had a synergistic effect on the action of chloride. In only one case did the added fluoride cause a failure of a verified threshold chloride-to sodium + silicate passing condition. The results of these tests are presented as:

Table 8 and Figure 9: -- Fluoride Added to Threshold Pass of Chloride with Sodium Orthosilicate
Table 8 and Figure 10: -- Fluoride Added to Threshold Pass of Chloride with Sodium Metasilicate

Long-Term Tests

The 84-day tests with fluoride alone (i.e without inhibitor) at 35, 175, 350, and 1500 mg/kg produced observable cracks at all concentrations except 35 mg/kg. The bromide and iodide tests were carried out using only 1500 mg/kg and produced pitting which was particularly severe with the bromide. One small crack was found on one of the two coupons tested with bromide, and on one of the two tested with iodide. The halide solutions were delivered to the coupons over each 28-day period after which the coupons were cleaned and inspected on the equipment, without being de-tensioned, then restarted. The cracks were observable only after the coupons were removed, flattened, cleaned, and re-bent and they may have been present before the end of the 84-day test period. The results of these tests are presented in Table 9A.

Combination Fluoride, Bromide, Iodide

Five concentrations (mg/kg) of the combination of fluoride, bromide and iodide respectively were tested for 28-days without inhibitors as follows: 1) 35,175,175; 2) 35,350,350; 3) 35,1500,1500; 4) 1500,175,175; 5) 1500,1500,1500. All four coupons tested at each combination had observable cracks. The results of these tests are presented in Table 9A.

28-Day Fluoride Tests

The finding that fluoride alone could promote ESCC in 84-days and that combinations with bromide and iodide resulted in ESCC after 28-days prompted additional fluoride tests for 28-days. Tests of fluoride alone at concentrations of 20, 35 and 100 mg/kg for 28 days produced cracking but 10 mg/kg for 28 days produced a verified pass. The results of these tests are presented in Table 9A.

Fluoride Inhibition

The inhibition of fluoride-induced ESCC was tested using both sodium orthosilicate and sodium metasilicate at the following fluoride-to-inhibitor concentrations (mg/kg); 50:100, 100:100, 200:200. Also tested was 200 mg/kg fluoride to100 mg/kg sodium orthosilicate inhibitor. Failures occurred with the 200 mg/kg fluoride to100 mg/kg sodium orthosilicate and the 100 mg/kg fluoride to100 mg/kg sodium metasilicate. The results of these tests are presented in Table 9B.

Bromide and Iodide Inhibition

Two hundred mg/kg bromide and 200 mg/kg iodide were each tested with 100 mg/kg sodium orthosilicate as the inhibitor. No cracks were found after inspection at the end of the 28-day test period. The results of these tests are presented in Table 9B.

DISCUSSION

Inhibitor Program Results vs. NRC RG 1.36 Acceptability Curve

This research indicated that the ratio of sodium + silicate-to-chloride at the low end of NRC RG 1.36 acceptability curve (Figure 1) is somewhat lower than required to completely prevent ESCC. Solution concentrations based on Figure 1 were chosen to identify both passing and failing conditions to establish a threshold-chloride pass which could be used for further testing with added fluoride. There were many failures at the beginning of the research because the tests used relatively high chloride concentrations. Subsequent testing found that at the lower end of the Figure 1 curve, (where the ratio of sodium + silicate and chloride is about 3:1), the threshold value is closer to 20:1. This indicates that a more uniform ratio exists over the full range of the curve.

Some small cracks were found using the dye-penetrant inspection and it is possible that the original Karnes' evaluation may have missed some very lightly cracked coupons in the low chloride portion of the acceptability curve. In addition, no specific information is provided about the carbon content of the metal Karnes used or whether there was one or more metal lots. Furthermore, Karnes' evaluation criteria of the four tested coupons allowed three passes and one failure to be considered acceptable. The current criteria of four passes results in some of the tests Karnes considered as acceptable to be plotted in the unacceptable region on the graph. These factors may account for the low ratio of sodium + silicate to chloride on the acceptability curve.

Some of the data from Karnes' report are summarized in Table 10 and plotted using a four pass - zero fail acceptance criteria in Figure 12. Three test points (#4, #6, and #11) appear very far from the acceptance curve and they all had low sodium content relative to the total sodium + silicate present. The verified threshold passes shown on Figure 8 indicate that low sodium-to-silicate ratios are farther below the Karnes curve than those with higher sodium content. This would suggest that Karnes' data and those developed in this study had strong similarities; i.e. the higher the percentage of sodium in the sodium silicate compound, the greater the effectiveness as an inhibitor.

Mole Ratio

The mole ratio of sodium-to-silicate had not been previously considered as a facet of ESCC inhibition. It is suspected that the initial authors of the guides assumed that the manufacturers would use sodium silicate compound to achieve the inhibiting effect. Karnes paper referred entirely to chloride versus "sodium + silicate compound." The results of this study indicate that there is a difference in the inhibitory effect for different mole ratios. The exact chloride-to-sodium + silicate acceptability thresholds have not been verified for all of the sodium-silicate mole ratios but it is clear that the mole ratio may be as important as the total quantity of sodium + silicate. In some cases the threshold-chloride pass conditions initially identified in this study did not pass the verification tests, indicating that the amount of inhibitor used was marginal and that slightly more inhibitor was required to attain a true threshold condition.

The summary of verified threshold passes shown on Figure 8 indicates, that when the sodium-to-silicate mole ratio declines from higher-to-lower sodium content, the mass ratio of sodium + silicate-to-chloride required to prevent ESCC increases. Sodium orthosilicate had the highest sodium-to-silicate ratio tested and it was most effective at inhibiting a given amount of chloride. Sodium disilicate had the lowest sodium-to-silicate ratio tested and it was least effective at inhibiting a given amount of chloride.

The threshold-passes obtained with potassium silicate compound (Figure 8) showed that significantly more silicate is required than when sodium is present. The limited data on sodium hydroxide shown on Figure 11, suggest that "all sodium" might be as effective as a "sodium + silicate" combination at inhibiting the ESCC action of chloride.

The two tests conducted with no chloride and 1000 and 5000 mg/kg sodium hydroxide, indicated that sodium hydroxide does not cause ESCC under the test conditions employed in this study.

Fluoride as an ESCC Promoter

It has been reported that a fluoride, bromide, or iodide solution applied at very high concentration for several months did not induce ESCC[5]. Other literature indicated that fluoride at lower concentrations might be more detrimental to stainless steel than high concentrations[6]. The cracks resulting from fluoride, bromide, and iodide in this study were generally very small and not the typical ESCC cracks observed with chloride. This may account for the reported absence of cracks with fluoride, bromide and iodide in Reference 5. It might also have been that the carbon content of the 304 stainless steel used in the test was low because it was not specified in the test method requirements. The current C 692 test method specifies a carbon content between 0.05 to 0.06 .

This research indicates that the concentrations of fluoride that may occur in insulation and accessories can cause ESCC, but that fluoride is much less aggressive than an equal amount of chloride. Fluoride-induced ESCC can be prevented with the same ions that inhibit chloride-induced ESCC, but at much lower concentrations. Provision for a minimum amount of sodium silicate should effectively eliminate any ESCC hazard from fluoride ions.

Verification Tests and Fluoride Addition To Threshold-Passes

The verification tests of all the threshold-passing conditions for chloride with sodium orthosilicate passed. Two of the sodium metasilicate - chloride verification tests failed but surprisingly the tests with added fluoride at those concentrations passed. The addition of fluoride to these threshold passes resulted in the failure of only 1 of 25 fluoride combinations tested. The condition failing was 100 mg/kg chloride : 1000 mg/kg sodium orthosilicate : 35 mg/kg fluoride. A retest of the failed condition with slightly lower chloride (80 mg/kg) resulted in a pass and suggests that the identified threshold value of chloride may have been slightly high.

While the above results indicated that fluoride may not be completely benign, it did not have a synergistic activating effect in combination with chloride. The concentrations of sodium orthosilicate or sodium metasilicate necessary to inhibit chloride-induced ESCC was sufficient to compensate for the addition of high and low concentrations of fluoride.

Combination Fluoride, Bromide, Iodide

Critical inspection indicated some cracking on all of the coupons exposed to a combination of fluoride, iodide, and bromide without any inhibitors. These cracks appeared different from those observed with chloride tested at these concentrations without an inhibitor, i.e., abundant transgranular cracking. The cracking generally had the appearance of surface crinkling that under 30x magnification must be legitimately called a crack (a few were rather definite).

Bromide and Iodide

Bromide and iodide test results indicate that these halogens are less aggressive than chloride and fluoride and that orthosilicate is effective as an inhibitor. These ions (bromide and iodide) are not widely found in insulation but may be found in mastics, glue, and facing. ASTM C 871 does not have specific tests for them, but by the nature of their chemistry bromide and iodide will increase the value obtained for chloride when using the amperometric-coulometric titration test method. The amount of inhibitor necessary for corrosion protection would be increased by this apparent increase in the chloride, thus compensating for the bromide and iodide.

CONCLUSIONS

1. In the absence of an inhibitor, chloride, fluoride, bromide, and iodide ions, alone or in combination, can cause ESCC of 304 stainless steel.
2. There appeared to be no synergistic effect attributable to the addition of fluoride ions to threshold chloride / sodium + silicate combinations.
3. The mole ratio of sodium-to-silicate had an effect on the inhibition of chloride-induced ESCC.
4. Inhibitors with high sodium-to-silicate ratios were the most effective. This means that the order of effectiveness for the sodium silicates that were tested is ortho>meta>di.
5. Based on minimal data, sodium hydroxide appears to function as an inhibitor.
6. Potassium silicate compound (all silicate) is significantly less effective as an inhibitor than the sodium silicate.
7. Many ESCC cracks were not visible unless the test coupon was flattened, re-bent, and examined using dye penetrant and 30x magnification.
8. ESCC cracking with fluoride, bromide, and iodide was not as severe as with chloride.
9. The coupons with long-term exposure to bromide and iodide without sodium silicate compound as an inhibitor had a crack and very pitted, particularly with bromide.
10. At the lower end of the Acceptability curve, Figure 1, where the ratio of sodium + silicate to chloride was about 3:1, the experimental value needed to obtain threshold passes approaches 20:1 for sodium orthosilicate. The ratios needed for the other sodium silicate compounds are somewhat higher.

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APPENDIX A

TABLES

TABLE 1

INHIBITOR SOLUTIONS

SODIUM ORTHOSILICATE (METSO 200*)
P.Q. SPECIFICATION SHEET ANALYSIS
Na_2O = 60.48%, SiO_2 = ~39.5%
CONCENTRATE SOLUTION PREPARED USING 30g IN 3 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Na = 4400 mg/l, SiO_3 = 3100 mg/l, TOTAL 7500 mg/l
Na = 58.7% OF TOTAL, SiO_3 = 41.3% OF TOTAL

SODIUM METASILICATE (METSO 2048*)
P.Q. SPECIFICATION SHEET ANALYSIS
Na_2O = 50.82%, SiO_2 = 46.55%
CONCENTRATE SOLUTION PREPARED USING 30.8g IN 3 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Na = 3700 mg/l, SiO_3 = 6000 mg/l, TOTAL 9700 mg/l
Na = 38.1% OF TOTAL, SiO_3 = 61.89% OF TOTAL

SODIUM DISILICATE (GD*)
P.Q. SPECIFICATION SHEET ANALYSIS
Na_2O = 26.41%, SiO_2 = ~52.82
CONCENTRATE SOLUTION PREPARED USING 37.9g IN 3 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Na = 2600 mg/l, SiO_3 = 8900 mg/l, TOTAL 11500 mg/l
Na = 22.6% OF TOTAL, SiO_3 = 77.4% OF TOTAL

POTASSIUM SILICATE (KASIL#6*)
P.Q. SPECIFICATION SHEET ANALYSIS
Na_2O = 0%, SiO_2 = 26.42%, K_2O = 12.58%
CONCENTRATE SOLUTION PREPARED USING 113.6g IN 3 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Na = 0 mg/l, SiO_3 = 10000 mg/l, TOTAL 10000 mg/l
Na = 0% OF TOTAL, SiO_3 = 100% OF TOTAL

SODIUM HYDROXIDE (BAKER ANALYZED)
NaOH = ~100%, SiO_2 = 0%
CONCENTRATE SOLUTION PREPARED USING 52.2g IN 3 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Na = 10000 mg/l, SiO_3 = 0 mg/l, TOTAL 10000 mg/l
Na = 100% OF TOTAL, SiO_3 = 0% OF TOTAL

* Obtained from P.Q. Corporation

TABLE 2

CHLORIDE, FLUORIDE, BROMIDE AND IODIDE SOLUTIONS

SOLUTION CONCENTRATIONS PREPARED FROM CERTIFIED SOURCE CHEMICALS

POTASSIUM CHLORIDE (KCl)
FORMULA WEIGHT = 74.56 (IAW*)
Cl = 35.5(IAW), = 47.6% OF TOTAL
K = 39.1(IAW), = 52.4% OF TOTAL
CONCENTRATE SOLUTION PREPARED USING 42g IN 2 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
Cl = 10000 mg/l

POTASSIUM FLUORIDE-DIHYDRATE ($KF\text{-}2\ H_20$)
FORMULA WEIGHT = 94.13 (IAW)
F = 19(IAW), = 20.18% OF TOTAL
$K\text{-}2\ H_20$ = 75.13(IAW), = 79.8% OF TOTAL
CONCENTRATE SOLUTION PREPARED USING 99.1g IN 2 LITERS

ASTM C 871 ANALYSIS OF CONCENTRATE SOLUTION
F = 10000 mg/l

POTASSIUM BROMIDE (KBr)
FORMULA WEIGHT = 119 (IAW)
Br = 79.9(IAW), = 67.1% OF TOTAL
K = 39.1(IAW), = 32.9% OF TOTAL
CONCENTRATE SOLUTION PREPARED USING 29.8g IN 2 LITERS

POTASSIUM IODIDE (KI)
FORMULA WEIGHT = 166 (IAW)
I = 126.91(IAW), = 76.45% OF TOTAL
K = 39.1(IAW), = 23.55% OF TOTAL
CONCENTRATE SOLUTION PREPARED USING 26.2g IN 2 LITERS

---

* International Atomic Weight

TABLE 3

SODIUM ORTHOSILICATE

%SiO_3=41.3%   %Na=58.7%

$NaSiO_3$/Cl ratio	Cl : $NaSiO_3$ (mg/kg)	SiO_3 (mg/kg)	Na (mg/kg)	PASS/FAIL
20	5 : 100	41.3	58.7	P/P/P/P
15	10 : 150	62	88	P/F
20	9 : 180	74.3	106	P/P
20	10 : 200	82.6	117	P/P/P/P
25	10 : 250	103	147	P/P
10	18 : 180	74.3	106	F/F
20	18 : 360	148.7	211	P/F
20	20 : 400	165.2	235	P/F
25	20 : 500	206.5	294	P/P/P/P
5	36 : 180	74.3	106	P/F
6.7	27 : 180	74.3	106	F/F
10	36 : 360	148.7	211	P/F
6.7	54 : 360	148.7	211	P/F
10	50 : 500	206.5	294	P/F
15	50 : 750	310	440	P/P/P/P
5	72 : 360	148.7	211	F/F
1.7	108 :180	74.3	106	F/F
7.5	100 :750	310	440	F/F
10	100 :1000	413	587	P/P/P/P
0.83	216 :180	74.3	106	F/F
2	180 :360	148.7	211	F/F
7.5	200 :1500	619.5	880	P/F
10	200 :2000	826	1174	P/P
12.5	200 :2500	1032	1468	P/P
1	360 :360	148.7	211	F/F
6	500 :3000	1239	1761	P/P
13.9	400 :5000	2065	2935	P/P
2.9	700 :2000	826	1174	F/F
7.1	700 :5000	2065	2935	P/P
12.8	700 :9000	3717	5283	P/P
14.3	700 :10-K	4130	5870	P/P

TABLE 4

SODIUM METASILICATE

$\%SiO_3=62\%$ $\%Na=38\%$

$NaSiO_3/Cl$ ratio	Cl : $NaSiO_3$ (mg/kg)	SiO_3 (mg/kg)	Na (mg/kg)	PASS/FAIL
33.3	3 :100	62	38	F/F/F/P/P/P
50	3 :150	93	57	P/P/P/P
20	9 :180	112	68	P/F
25	10 :250	155	95	P/P
10	18 :180	112	68	F/F
20	18 :360	223	137	P/P
20	20 :400	248	152	P/P/P/P
30	20 :600	372	228	P/F/P/P/P/P
5	36 :180	112	68	F/F
6.7	27 :180	112	68	P/F
10	36 :360	223	137	P/F
20	30 :600	372	228	P/P
6.7	54 :360	223	137	P/F
15	50 :750	465	285	P/F
20	50 :1000	620	380	P/P/P/F
30	50 :1500	930	570	P/P/P/P
5	72 :360	223	137	P/F
1.7	108 :180	112	68	F/F
10	100 :1000	620	380	F/F
15	100 :1500	930	570	P/P/P/P
20	100 :2000	1240	760	P/P/P/F
0.83	216 :180	112	68	F/F
2	180 :360	223	137	F/F
10	200 :2000	1240	760	P/F
12.5	200 :2500	1550	950	P/P/F/F
17.5	200 :3500	2170	1330	P/P/F/F
1	360 :360	223	137	F/F
6	500 :3000	1860	1140	P/F
14	350 :5000	3100	1900	P/P/P/P
7.1	700 :5000	3100	1900	P/P/P/F
12.9	700 :9000	5580	3420	P/P
14.3	700 :10000	6200	3800	P/P

TABLE 5

SODIUM DISILICATE

%SiO$_3$=77.4% %Na=22.6%

NaSiO$_3$/Cl ratio	Cl : NaSiO$_3$ (mg/kg)	SiO$_3$ (mg/kg)	Na (mg/kg)	PASS/FAIL
33.3	3 : 100	77	23	P/P/P/P
20	9 : 180	139	41	F/F
25	10 : 250	194	56	P/F
40	10 : 400	310	90	P/PF/F
10	18 : 180	139	41	P/F
20	18 : 360	279	81	P/P
20	20 : 400	310	90	P/P/F/F
50	20 : 1000	774	226	P/P/P/P
5	36 : 180	139	41	F/F
6.7	27 : 180	139	41	F/F
10	36 : 360	279	81	P/F
33.3	30 : 1000	774	226	F/F
6.7	54 : 360	279	81	P/F
20	50 : 1000	774	226	F/F
40	50 : 2000	1548	452	P/P/P/P
5	72 : 360	279	81	F/F
27	75 : 2000	1548	452	F/F
1.7	108 :180	139	41	F/F
10	100 :1000	774	226	F/F
15	100 :1500	1161	339	F/F
20	100 :2000	1548	452	F/F
30	100 :3000	2322	678	F/F
40	100 :4000	3096	904	P/P/F/F
0.83	216 :180	139	41	F/F
2	180 :360	279	81	F/F
12.5	200 :2500	1935	565	P/F
17.5	200 :3500	2709	791	P/P
23.3	150 :3500	2709	791	F/F
1	360 :360	279	81	F/F
25	400 :10000	7740	2260	P/P/P/P
16.7	600 :10000	7740	2260	F/F
14.3	700 :10000	7740	2260	P/F

TABLE 6

POTASSIUM SILICATE

%SiO_3=100% %Na=0%

$NaSiO_3$/Cl ratio	Cl : $NaSiO_3$ (mg/kg)	SiO_3 (mg/kg)	Na (mg/kg)	PASS/FAIL
33.3	3 : 100	100	0	P/P/P/P
20	9 : 180	180	0	P/F
25	10 : 250	250	0	F/F
50	10 : 500	500	0	P/P
60	10 : 600	600	0	P/F
10	18 : 180	180	0	F/F
20	18 : 360	360	0	P/F
22.5	20 : 450	450	0	F/F
100	20 : 2000	2000	0	P/F
150	20 : 3000	3000	0	P/P/P/P
6.7	27 : 180	180	0	P/F
66.7	30 : 2000	2000	0	P/F
10	36 : 360	360	0	P/F
20	50 : 1000	1000	0	F/F
6.7	54 : 360	360	0	P/F
10	100 : 1000	1000	0	P/F/F/F/P/P
40	100 : 4000	4000	0	P/P/P/P
12.5	200 : 2500	2500	0	F/F
17.5	200 : 3500	3500	0	P/F
22.5	200 : 4500	4500	0	P/F
30	200 : 6000	6000	0	P/P
16.7	600 : 10000	10000	0	P/P/P/P
14.3	700 : 10000	10000	0	F/F

TABLE 7
SODIUM HYDROXIDE
%SiO3=0% %Na=100%

Na/Cl ratio	Cl : Na (mg/kg)	SiO_3 (mg/kg)	Na (mg/kg)	PASS/FAIL
0	0 : 1000	0	1000	P
0	0 : 5000	0	5000	P
10	10 : 100	0	100	P/F
30	10 : 300	0	300	P
100	10 : 1000	0	1000	P
500	10 : 5000	0	5000	P
5	20 : 100	0	100	P
15	20 : 300	0	300	P/F
25	20 : 500	0	500	P/F
6	50 : 300	0	300	F
12	50 : 600	0	600	F/F
16	50 : 800	0	800	P/P
6	100 : 600	0	600	F
10	100 : 1000	0	1000	P/P/P/P
3.3	300 : 1000	0	1000	P
6	500 : 3000	0	3000	P/P

TABLE 8

VERIFIED THRESHOLD PASS OF CHLORIDE : SODIUM ORTHOSILICATE + ADDED FLUORIDE

Cl : ORTHO (mg/kg)	+ F (mg/kg)	PASS/FAIL
5 : 100	+ 20	P/P
	+ 70	P/P
	+ 100	P/P
10 : 200	+ 35	P/P
	+ 175	P/P
	+ 350	P/P
	+ 1500	P/P
20 : 500	+ 35	P/P
	+ 175	P/P
	+ 350	P/P
	+ 1500	P/P
50 : 750	+ 35	P/P
	+ 175	P/P
	+ 350	P/P
	+ 1500	P/P
80 : 1000	+ 35	P/P
100: 1000	+ 35	P/F/P/F
	+ 175	P/P
	+ 350	P/P
	+ 1500	P/P

CHLORIDE : SODIUM METASILICATE + ADDED FLUORIDE

Cl : META (mg/kg)	+F (mg/kg)	PASS/FAIL
3 : 100	+ 20	P/P
	+ 70	P/P
	+ 150	P/P
10 : 300	+ 30	P/P
	+ 60	P/P
	+ 100	P/P
	+ 1500	P/P
100: 2000	+ 200	P/P
	+ 400	P/P
	+ 1500	P/P
700: 5000	+ 1500	P/P

TABLE 9A

QUALIFICATION OF METAL WITH DI WATER

DAYS EXPOSED	FLUORIDE (mg/kg)	BROMIDE (mg/kg)	IODIDE (mg/kg)	PASS/FAIL
84	0	0	0	P/P
28	0	0	0	P/P

INDIVIDUAL FLUORIDE, BROMIDE, AND IODIDE (WITHOUT INHIBITOR)

DAYS EXPOSED	FLUORIDE (mg/kg)	BROMIDE (mg/kg)	IODIDE (mg/kg)	PASS/FAIL
84	35	0	0	P/P
84	175	0	0	P/F
84	350	0	0	P/F
84	1500	0	0	P/F
56	0	1500	0	P/F *
56	0	0	1500	P/F **

* Many pits. One crack.

** Many pits but less than with bromide. One crack.

FLUORIDE, BROMIDE, IODIDE COMBINATIONS (WITHOUT INHIBITOR)

DAYS EXPOSED	FLUORIDE (mg/kg)	BROMIDE (mg/kg)	IODIDE (mg/kg)	PASS/FAIL
28	35	175	175	F/F/F/F
	35	350	350	F/F/F/F
	35	1500	1500	F/F/F/F
	1500	175	175	F/F/F/F
	1500	1500	1500	F/F/F/F

1 MONTH FLUORIDE (WITHOUT INHIBITOR)

DAYS EXPOSED	FLUORIDE (mg/kg)	BROMIDE (mg/kg)	IODIDE (mg/kg)	PASS/FAIL
28	10			P/P/P/P
	20			P/F
	35			P/F
	100			P/F/F/F

TABLE 9B

FLUORIDE WITH SODIUM ORTHOSILICATE INHIBITOR

DAYS EXPOSED	FLUORIDE + (mg/kg)	SODIUM ORTHOSILICATE (mg/kg)	PASS/FAIL
28	50	100	P/P
	100	100	P/P
	200	200	P/P
	200	100	F/F

FLUORIDE WITH SODIUM METASILICATE INHIBITOR

DAYS EXPOSED	FLUORIDE + (mg/kg)	SODIUM METASILICATE (mg/kg)	PASS/FAIL
28	50	100	P/P
	100	100	P/F
	200	200	P/P

200 BROMIDE + 100 SODIUM ORTHOSILICATE INHIBITOR

DAYS EXPOSED	BROMIDE + (mg/kg)	SODIUM ORTHOSILICATE (mg/kg)	PASS/FAIL
28	200	100	P/P

200 IODIDE + 100 SODIUM ORTHOSILICATE INHIBITOR

DAYS EXPOSED	IODIDE + (mg/kg)	SODIUM ORTHOSILICATE (mg/kg)	PASS/FAIL
28	200	100	P/P

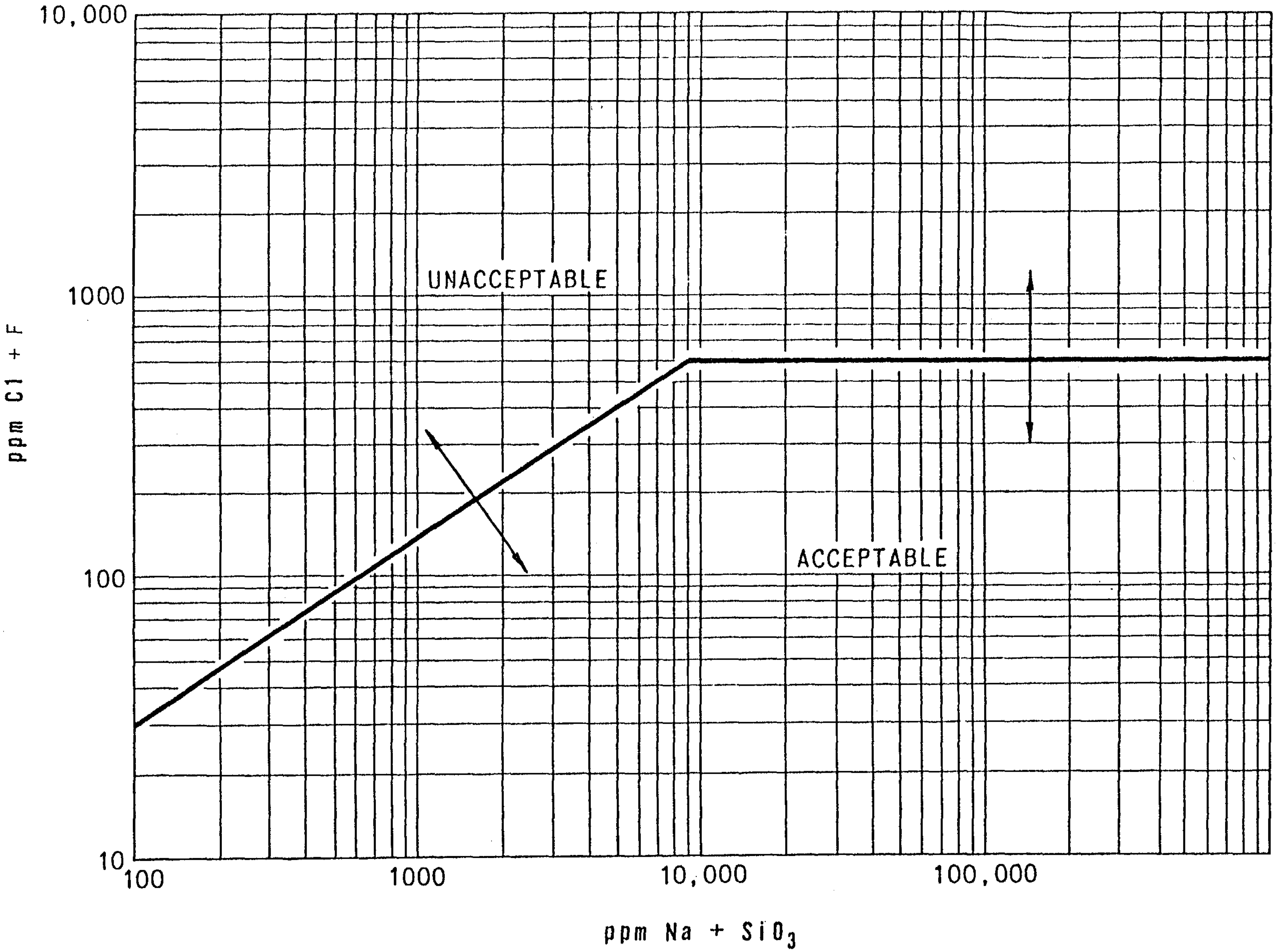
TABLE 10

SELECTED DATA FROM KARNES PAPER

TEST #	Cl mg/kg	SiO3 mg/kg	Na mg/kg	FAILED #	Na+SiO3 mg/kg	PASS [Cl Content	FAIL (mg/kg)]	SiO3 %	Na %
1	95	10300	4000	0	14300	95		72.02797	27.97203
2	275	5600	500	0	6100	275		91.80328	8.196721
3	285	5150	700	1	5850		285	88.03419	11.96581
4	40	7600	80	1	7680		40	98.95833	1.041667
5	420	3600	700	3	4300		420	83.72093	16.27907
6	25	1300	140	3	1440		25	90.27778	9.722222
7	45	650	70	0	720	45		90.27778	9.722222
8	24	140	80	0	220	24		63.63636	36.36364
9	28	300	150	1	450		28	66.66667	33.33333
10	200	65	200	0	265	200		24.5283	75.4717
11	5	280	70	3	350		5	80	20
12	15	110	90	0	200	15		55	45
13	25	68	100	0	168	25		40.47619	59.52381
14	530	130	400	4	530		530	24.5283	75.4717
15	280	160	200	4	360		280	44.44444	55.55556
16	490	110	300	3	410		490	26.82927	73.17073
17	20	120	20	0	140	20		85.71429	14.28571
18	20	65	70	0	135	20		48.14815	51.85185
19	1110	38	70	4	108		1110	35.18519	64.81481
20	1240	68	200	4	268		1240	25.37313	74.62687
21	15	30	160	0	190	15		15.78947	84.21053
22	118	30	10	2	40		118	75	25
23	5	190	5	0	195	5		97.4359	2.564103
24	360	35	100	4	135		360	25.92593	74.07407
25	250	1080	100	3	1180		250	91.52542	8.474576
26	380	3800	3000	0	6800	380		55.88235	44.11765
27	180	1940	2700	0	4640	180		41.81034	58.18966
28	290	4340	4000	0	8340	290		52.03837	47.96163
29	275	2170	5000	0	7170	275		30.26499	69.73501
30	130	300	600	4	900		130	33.33333	66.66667
31	63	829	300	1	1129		63	73.42781	26.57219
32	560	68	400	2	468		560	14.52991	85.47009
33	130	3500		0	3500	130		100	0
34	285	470	660	3	1130		285	41.59292	58.40708
35	26	2200	2100	0	4300	26		51.16279	48.83721
36	110	270	2100	6	2370		110	11.39241	88.60759
37	23	79	170	1	249		23	31.72691	68.27309
38	6	11	1700	0	1711	6		0.642899	99.3571
39	10	430	10	0	440	10		97.72727	2.272727
40	7	870	100	0	970	7		89.69072	10.30928
41	11	1100	100	0	1200	11		91.66667	8.333333
42	280	5720	1240	4	6960		280	82.18391	17.81609
43	250	140	220	3	360		250	38.88889	61.11111
44	350	3940	2980	0	6920	350		56.93642	43.06358
45	251	2370	1790	0	4160	251		56.97115	43.02885

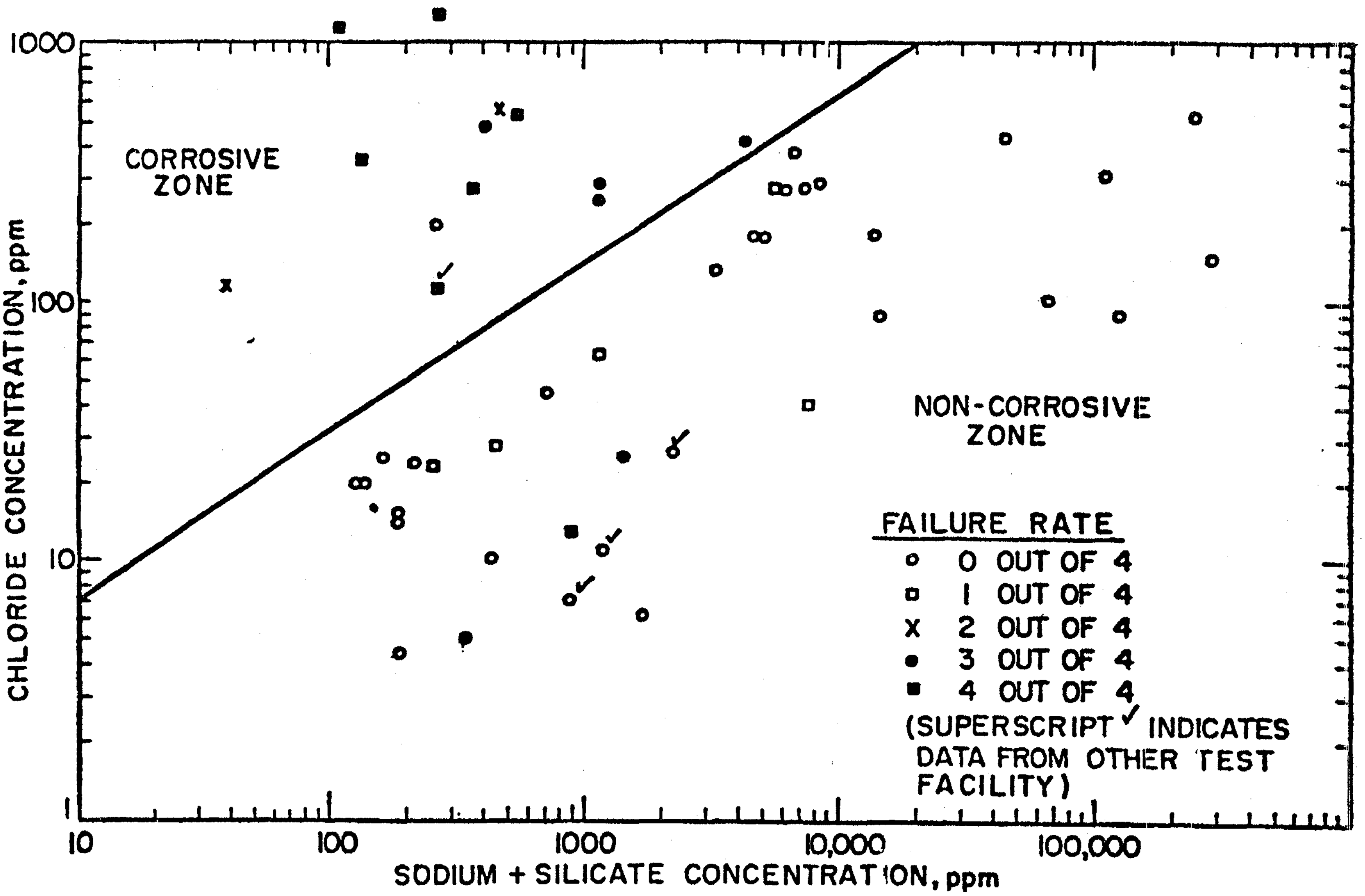
APPENDIX B

FIGURES



ACCEPTABILITY OF INSULATION MATERIAL BASED ON THE LEACHABLE (Cl + F) AND THE LEACHABLE (Na + SiO_3) ANALYSES

FIGURE 1



FAILURE RATE AS FUNCTION OF CHLORIDE, SODIUM AND SILICATE COMPOUND

FIGURE 2

RELATIONSHIP BETWEEN LEACHABLE ION CONTENT OF INSULATION (Y1) VS. THE TOTAL AMOUNT DELIVERED TO THE COUPON (X1) VS. THE CONCENTRATION IN THE SIMULATED EXTRACTION SOLUTION (Y2)

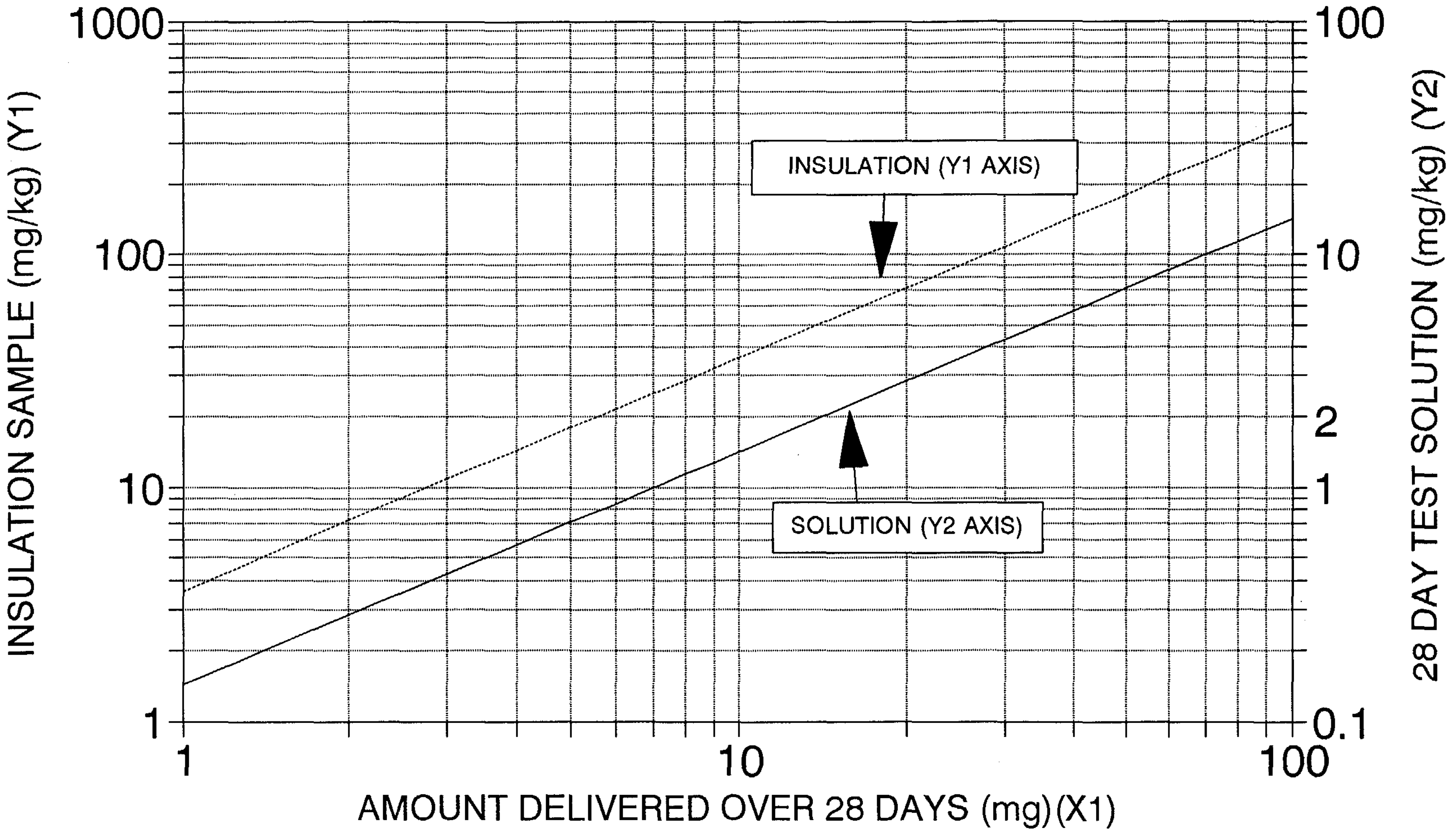


Figure 3

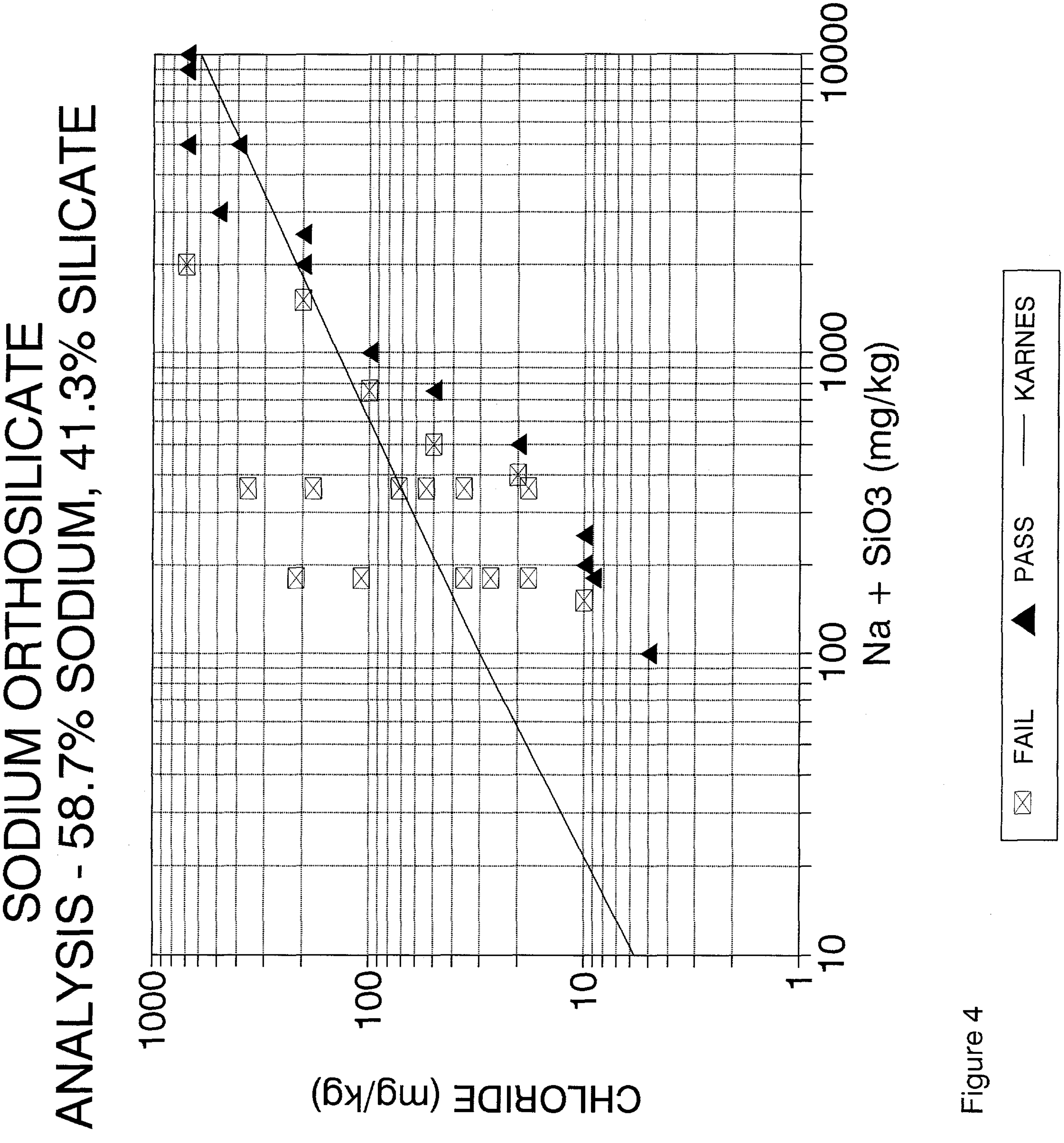

SODIUM ORTHOSILICATE
ANALYSIS - 58.7% SODIUM, 41.3% SILICATE
CHLORIDE (mg/kg)
1000
100
10
1
10
100
1000
10000
Na + SiO3 (mg/kg)
☒ FAIL
▲ PASS
— KARNES

Figure 4

SODIUM METASILICATE
ANALYSIS - 38% SODIUM, 62% SILICATE

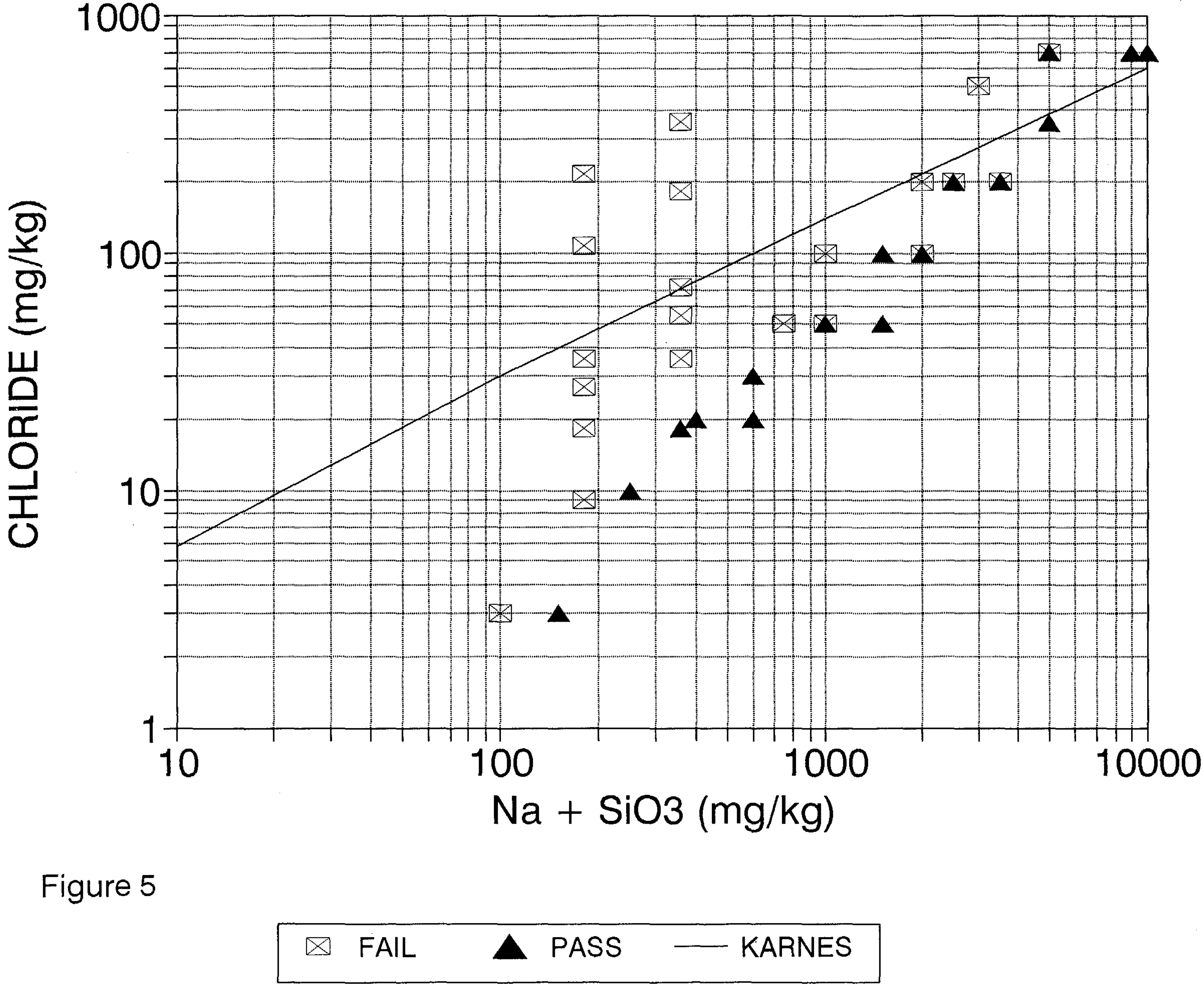


Figure 5

SODIUM DISILICATE
ANALYSIS - 22.6% SODIUM, 77.4% SILICATE

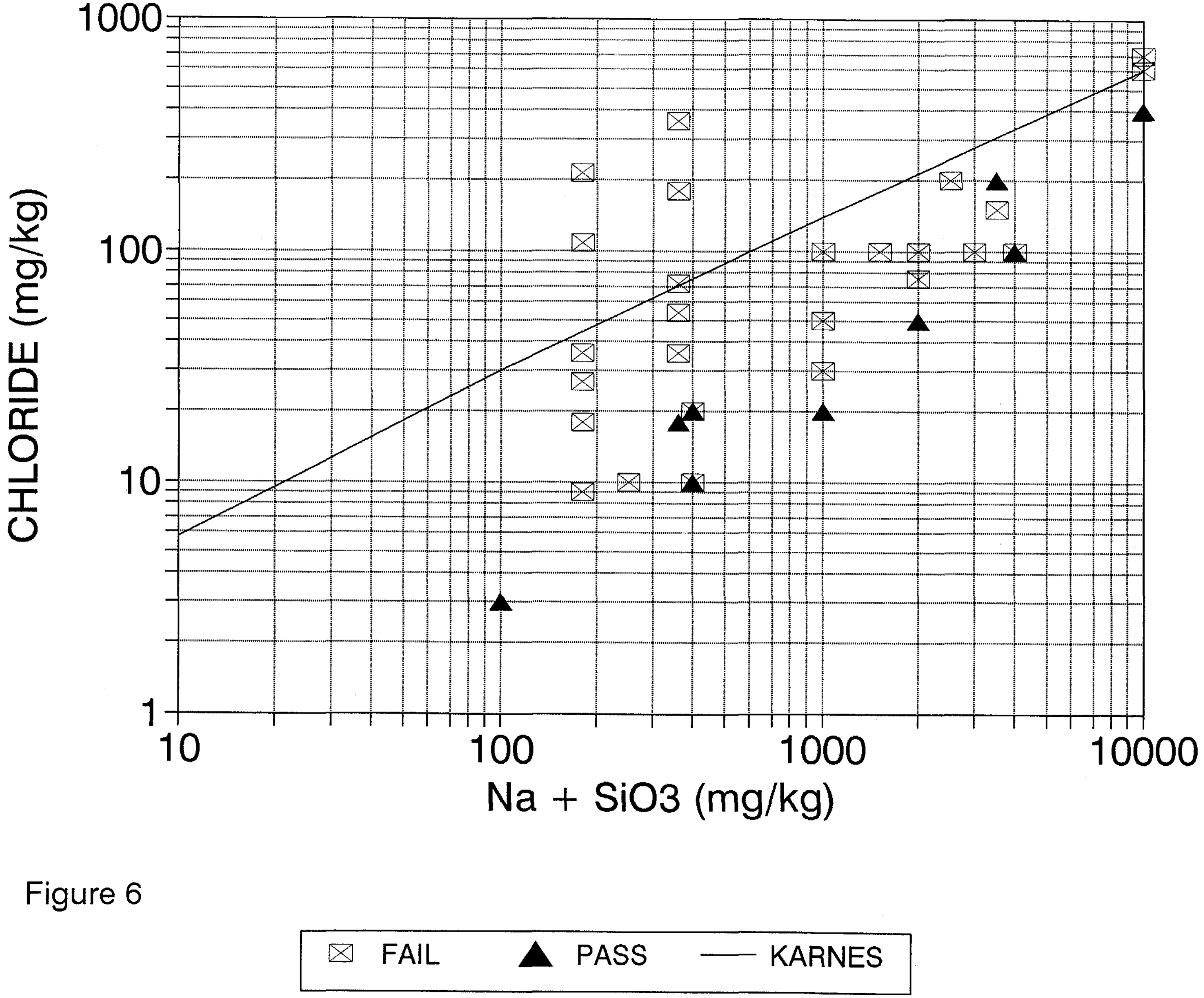


Figure 6

POTASSIUM SILICATE
ANALYSIS - 0% SODIUM, 100% SILICATE

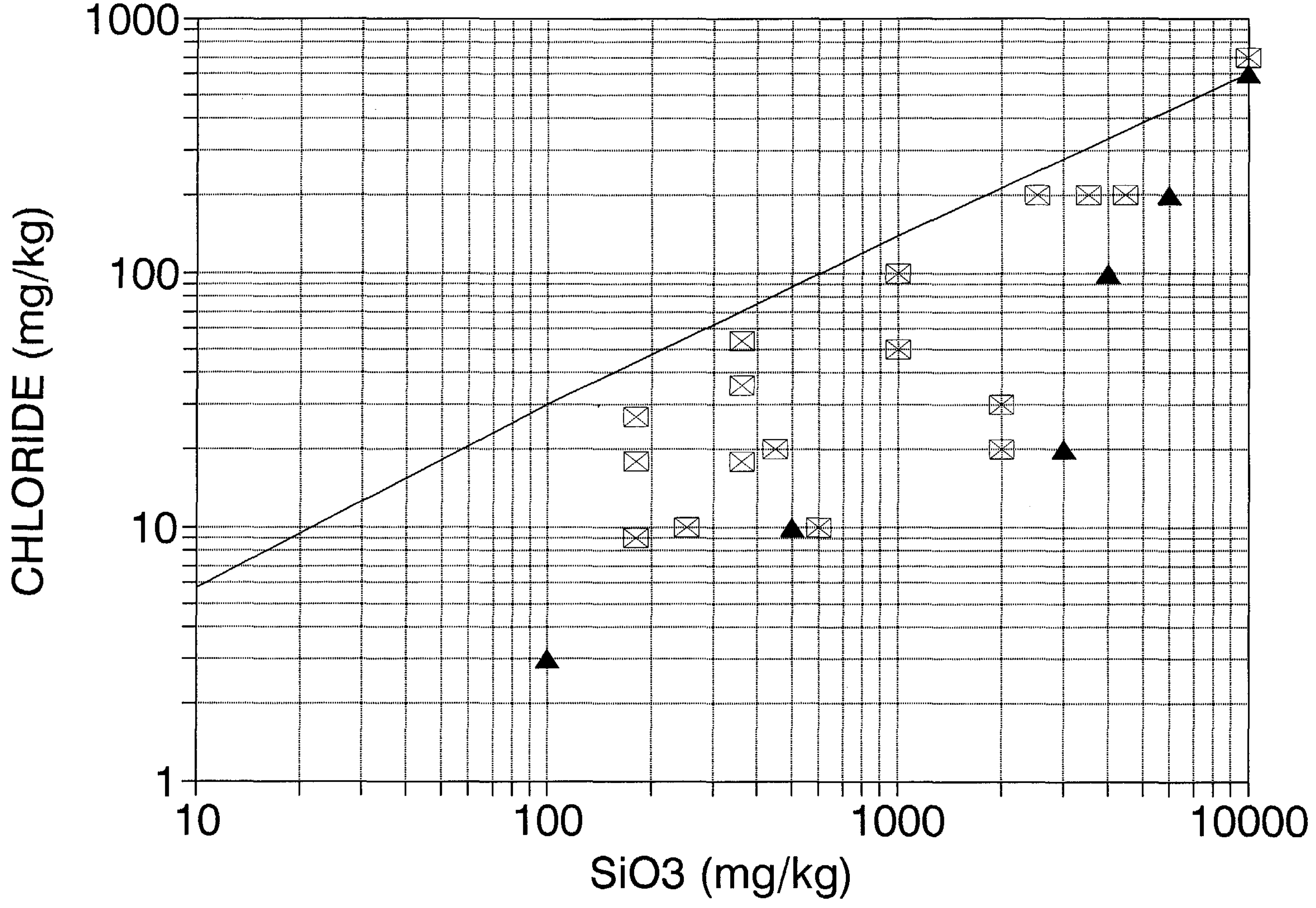


Figure 7

VERIFIED THRESHOLD PASSES FOR DIFFERENT SODIUM-TO-SILICATE RATIOS

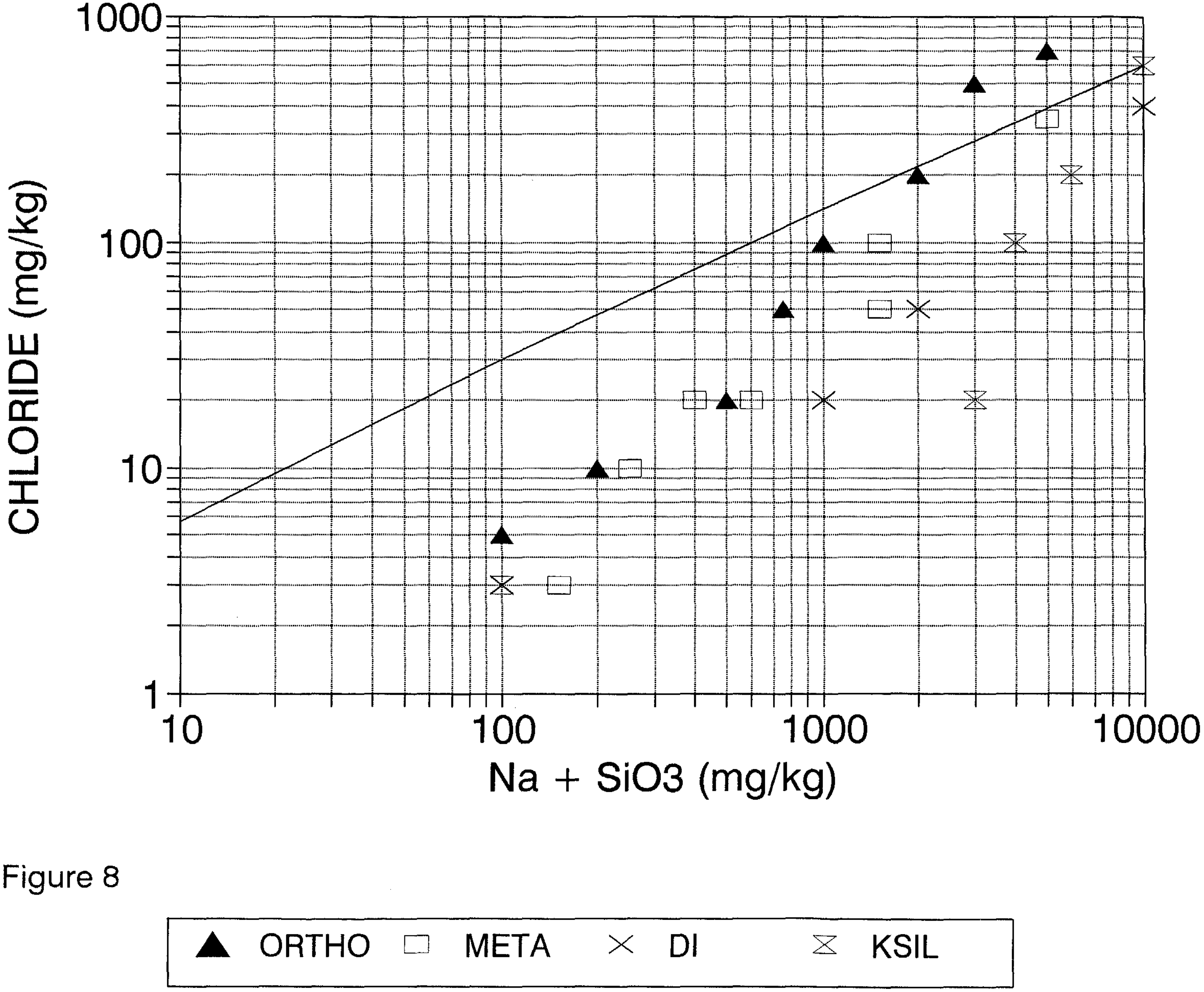


Figure 8

FLUORIDE ADDED TO THRESHOLD PASS OF CHLORIDE WITH SODIUM ORTHOSILICATE

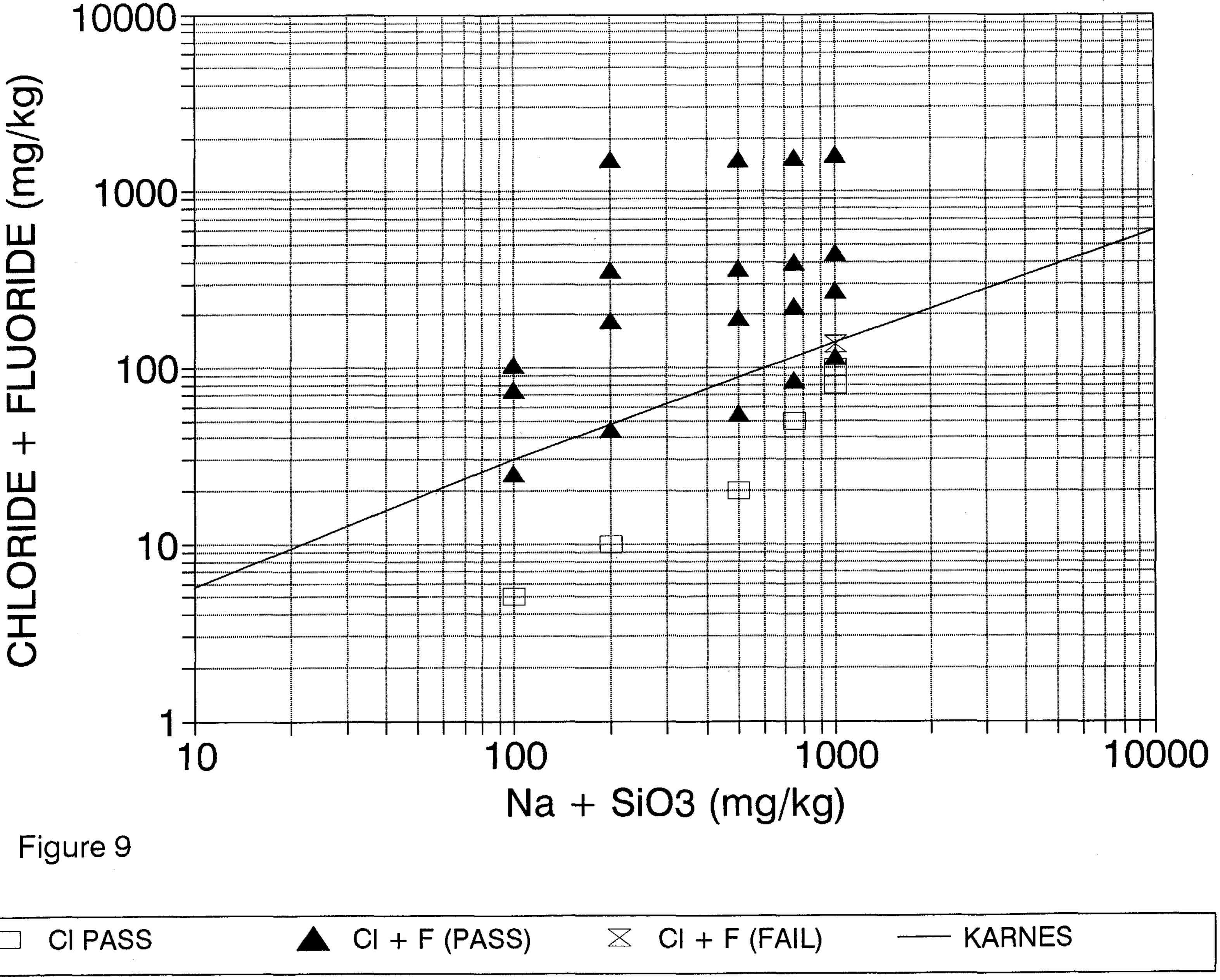


Figure 9

FLUORIDE ADDED TO THRESHOLD PASS OF CHLORIDE WITH SODIUM METASILICATE

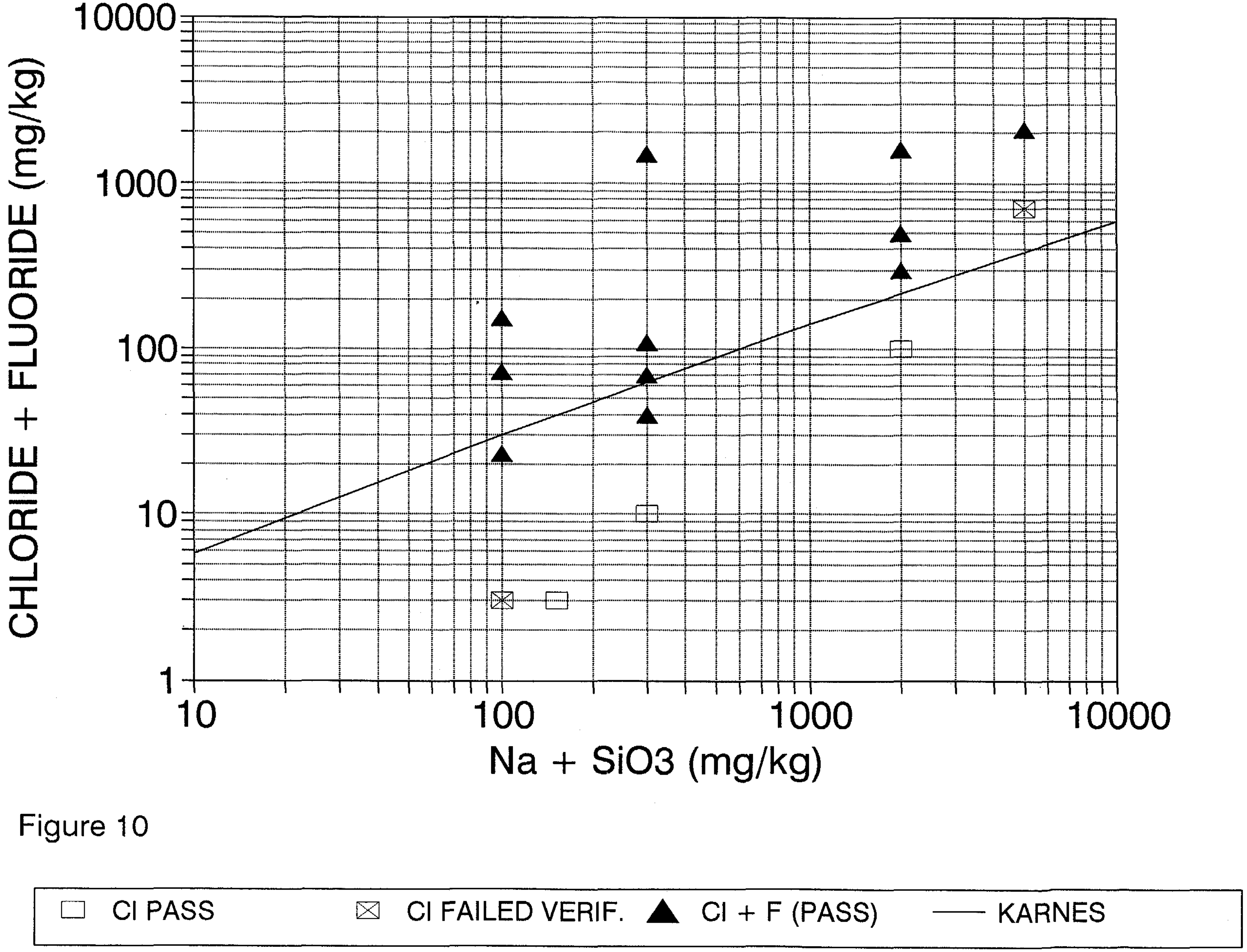


Figure 10

SODIUM HYDROXIDE
ANALYSIS - 100% SODIUM, 0% SILICATE

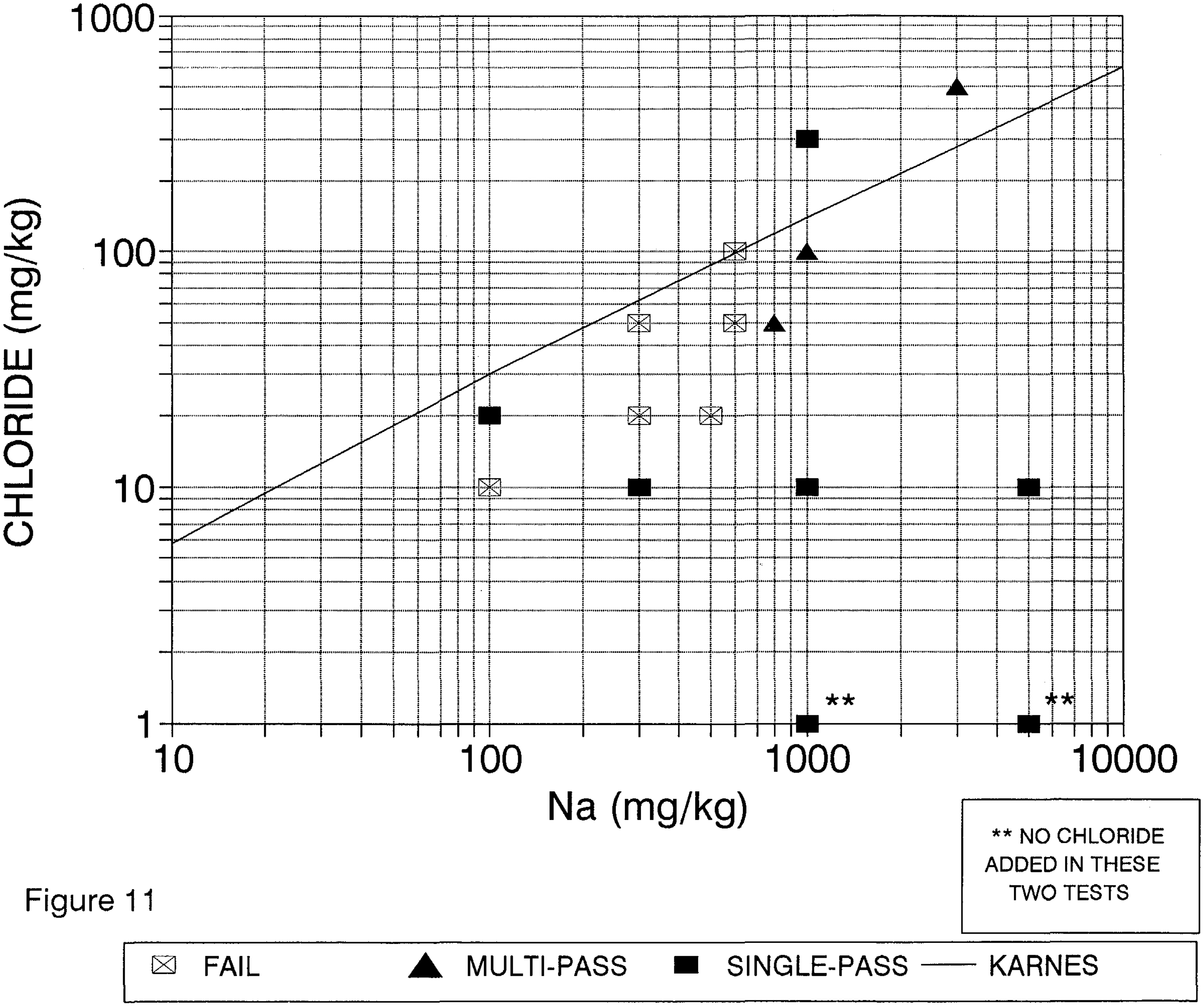


Figure 11

RE-PLOT OF SELECTED KARNES DATA USING ZERO FAILURES REQUIRED TO PASS *

*COMPARE TO FIGURE 2

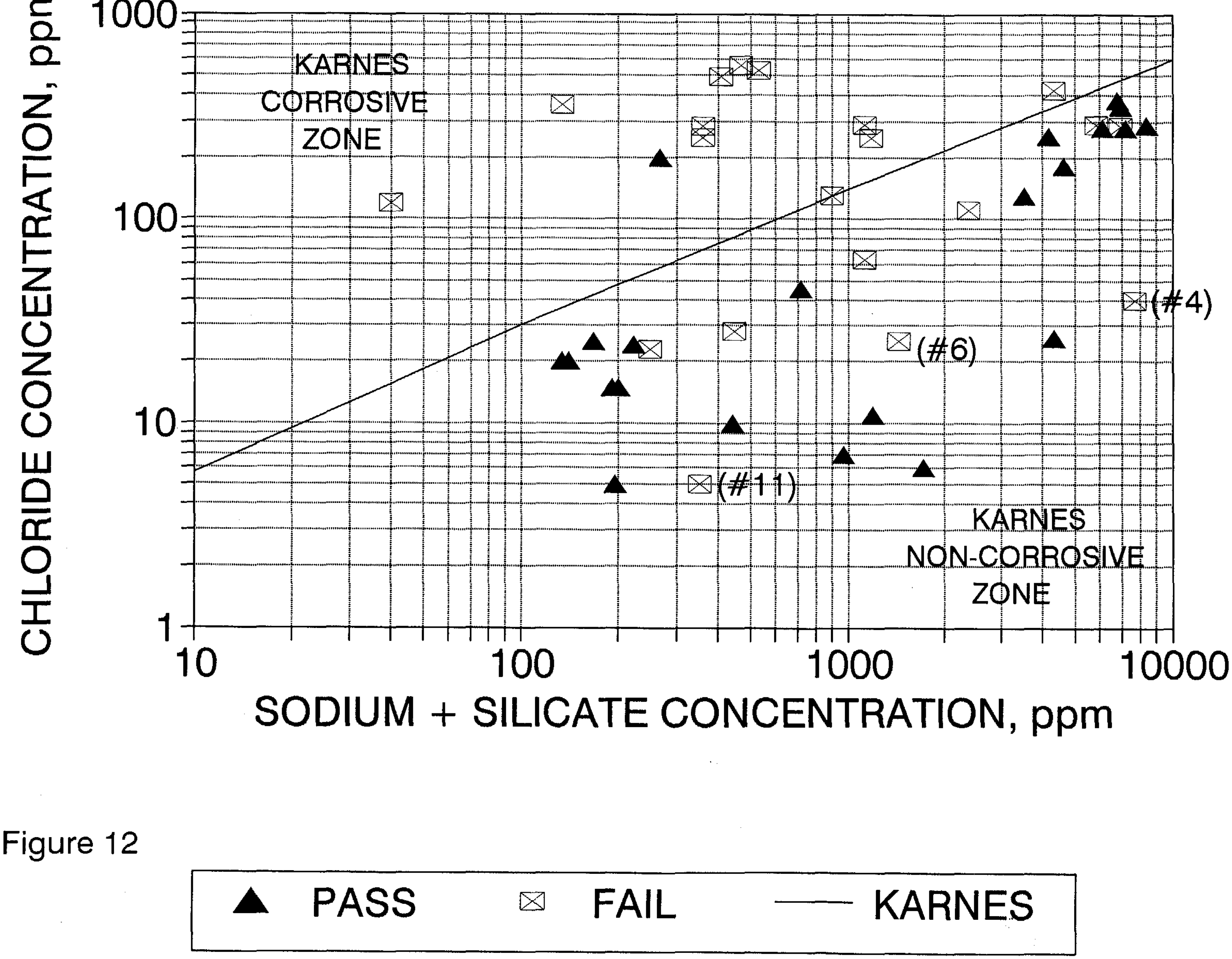


Figure 12

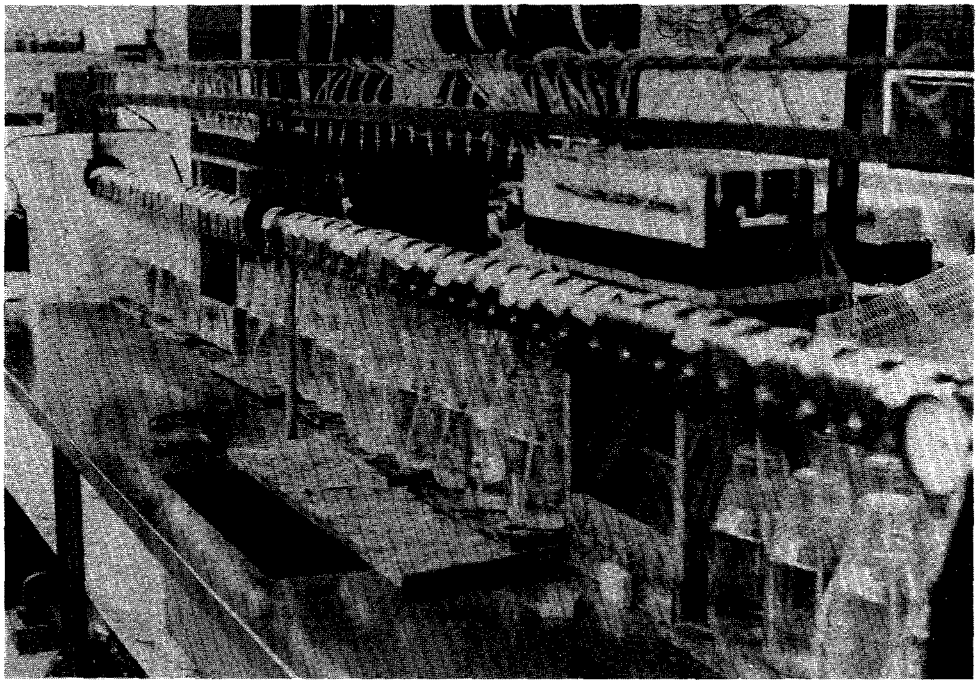


IMAGE 1
LAB SETUP OF ASTM C692 TEST EQUIPMENT
WITH 48 TEST COUPONS

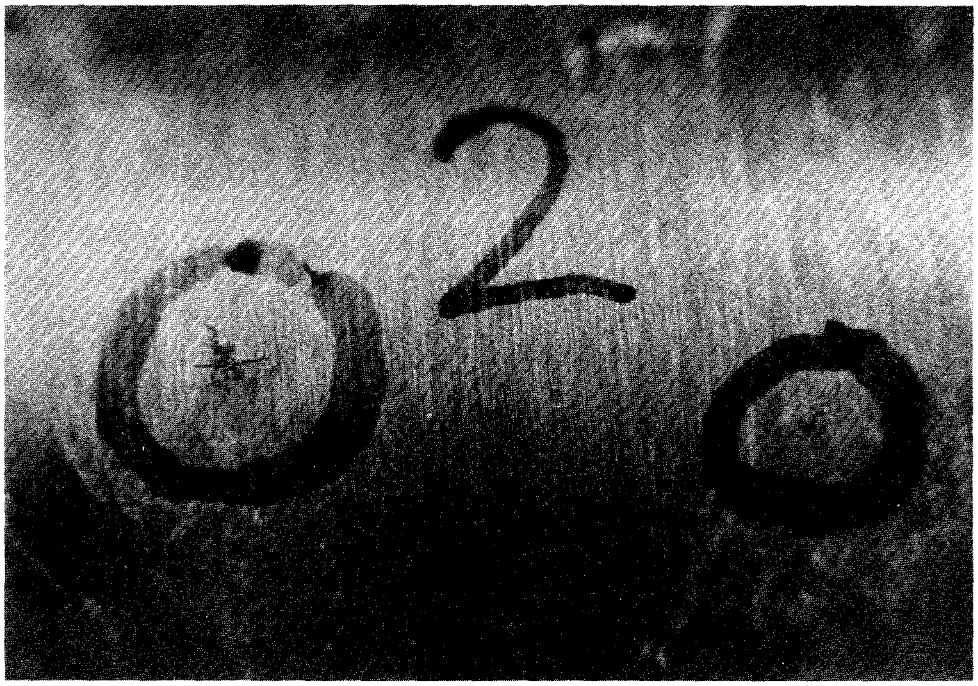


IMAGE 2 - 7X
TYPICAL DENDRITIC ESCC CRACKING
SMALL, BARELY DISCERNABLE CRACKS

IMAGE 3 - 7X
MEDIUM SIZE DENDRITIC ESCC ON LEFT
SMALL CRACK ON RIGHT, BARELY DISCERNABLE BUT
CONFIRMED USING DYE PENETRANT
AND VERIFIED UNDER 30X MAGNIFICATION

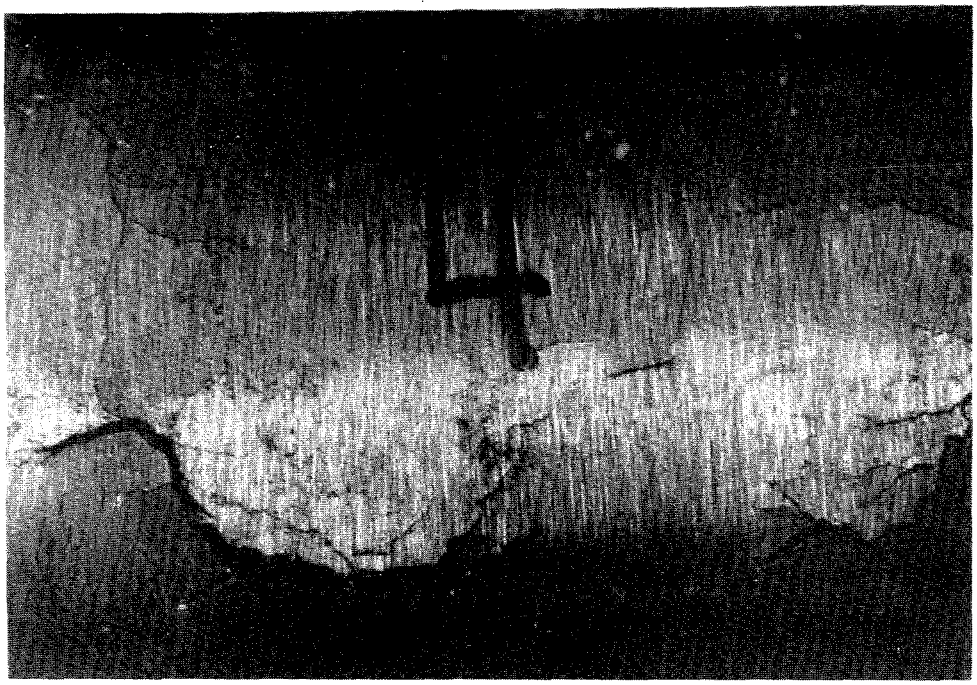


IMAGE 4 - 7X
CATASTROPHIC ESCC TYPICAL WHEN CHLORIDE
CONCENTRATION IS GREATER THAN 200 mg/kg IN INSULATION
WITHOUT ANY SODIUM + SILICATE INHIBITION

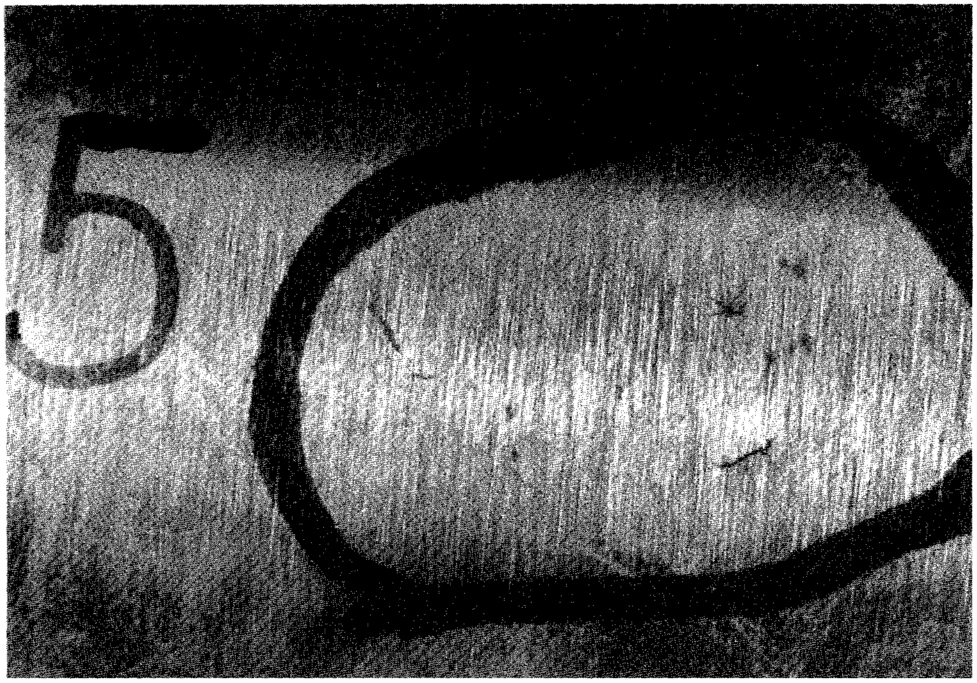


IMAGE 5 - 7X
FLUORIDE CRACK. NOT FOUND BY EYE BUT
PICKED UP USING DYE PENETRANT

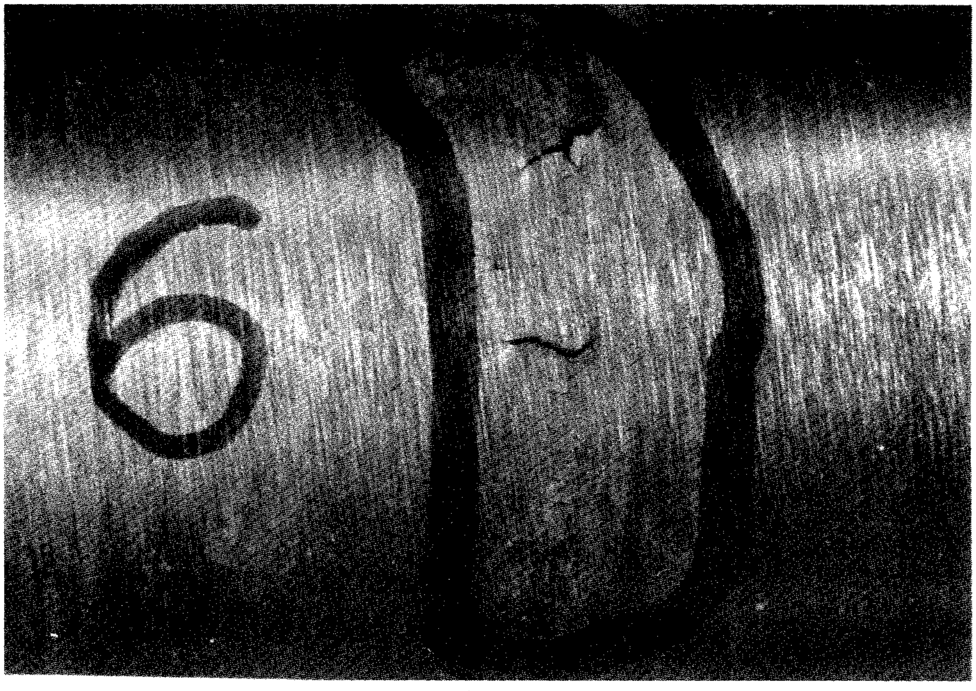


IMAGE 6 - 7X
TYPICAL SMALL ESCC CRACKS
VISIBLE BY EYE AND DYE PENETRANT

NRC FORM 335
(2-89)
NRCM 1102,
3201, 3202

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10. SUPPLEMENTARY NOTES
E. Woolridge, NRC Project Manager

11. ABSTRACT *(200 words or less)*

The drip procedure from ASTM C 692-95a was used to research the effect of halogens and inhibitors on the External Stress Corrosion Cracking (ESCC) of Type 304 stainless steel as it applies to NRC RG 1.36. The solutions used in this research were prepared using pure chemical reagents to simulate the halogens and inhibitors found in insulation extraction solutions.

The results indicated that sodium silicate compounds that were higher in sodium were more effective for preventing chloride-induced ESCC in type 304 austenitic stainless steel. Potassium silicate (all-silicate inhibitor) was not as effective as sodium silicate. Limited testing with sodium hydroxide (all-sodium inhibitor) indicated that it may be effective as an inhibitor.

Fluoride, bromide, and iodide caused minimal ESCC which could be effectively inhibited by sodium silicate. The addition of fluoride to the chloride/sodium silicate systems at the threshold of ESCC appeared to have no synergistic effect on ESCC. The mass ratio of sodium + silicate (mg/kg) to chloride (mg/kg) at the lower end of the NRC RG 1.36 Acceptability Curve was not sufficient to prevent ESCC using the methods of this research.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

External stress corrosion cracking, ESCC, stress corrosion, SCC, sodium silicate, chloride, fluoride, bromide, iodide, thermal insulation, austenitic stainless steel, type 304 stainless steel, inhibition, ASTM C 692, Regulatory Guide 1.36, MIL-I-24244

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