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CORROSION INHIBITION

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The present invention relates in general to the protection of ferrous metals from the corrosive action of aqueous solutions, and more particularly to a novel method for inhibiting such corrosion by the incorporation of small amounts of certain additive agents into the aqueous solutions.

As is known, the vexing problem of curbing and mitigating the pernicious progressive corrosion of ferrous metal vessels and apparatus by aqueous solutions in contact therewith is of virtually universal occurrence and concern throughout the art. Notoriously deleterious, such corrosion results in the gradual destructive disintegration of the metal apparatus and in the contamination of the solutions with the corrosion products; in addition, as the corrosion mechanism involved is essentially the progressive oxidation of metallic iron, adverse reduction of solutes in the solutions as a concomitant to the oxidation occasionally proves serious. Rate and severity of corrosion ordinarily vary with the particular type of ferrous metal involved, with carbon steel normally suffering attack at a greater rate than electrolytic iron or the stainless steels. Too, aqueous solutions of strong electrolytes—aqueous strong acids, bases, and salts, such as chlorides and sulfates—are usually more corrosive than plain water. Furthermore, elevated temperatures generally serve to accelerate corrosion rates prodigiously.

In the past, one method rather widely applied toward mitigating such corrosion has comprised of incorporating chromate or dichromate ions in the aqueous solutions. When present in solution in sufficient concentration, the chromate and dichromate ions have shown themselves able to render the ferrous metal surfaces largely non-reactive with aqueous solutions and to retain the surfaces continuously in such inactive state; appropriate minimum chromate concentrations are, for protection of iron, machine, and carbon steel, something of the order of 0.05 to 0.1% (by weight) chromate for plain water at 20° C., 0.2% for plain water at 80° to 90° C., and up to 1% or more in the presence of aqueous strong electrolytes such as 100–300 milligrams per liter of chlorides. The protection then afforded has been attributed to various mechanisms. For instance, one view postulates that the function of the chromate (or dichromate) ions is to “heal” breaches in a fragile protective film of ferric oxide which is formed on the metal surface by incipient corrosive reaction; purportedly the chromate reacts to build-out from the broken edges of the ferric oxide film so as to form a “scar” film across the breach—perhaps via reduction of chromate ions to Cr^{+3} in redox reaction with Fe^0 , or Fe^{++} formed below the corroding “breaches” in the film. Other views propound a dynamic “secondary valence” attachment of chromate or dichromate ions

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only to those metal atoms of particular reactivity on the metal surface, or alternatively a dynamic chemisorption (i. e., anion-exchange adsorption) of chromate ions upon the metal surface—whereupon, in either case, the chromate or dichromate radicals shield reactive sites on the metal surface from oxide formation. For further information as to prior art inhibition of ferrous metal corrosion with chromates and dichromates, reference may be made to U. R. Evans, “Metallic Corrosion Passivity and Protection,” second edition, Longman’s Green and Company, New York, 1948.

While use of chromates and dichromates for inhibition of ferrous metal corrosion has been broadly successful in practice, it nevertheless has not proven to be unqualifiedly satisfactory for the purpose. Especially in the chemical processing industries, it is recognized as particularly desirable to curtail the necessary concentration of inhibitory agent as much as practicable. Aside from corrosion-inhibition service, the presence of any substantial concentration of inhibitory reagent such as chromate is commonly undesirable, not only because it represents a significant impurity, but also because of the possibility of its engaging in process-disruptive side-reactions or catalysis. Furthermore, in the atomic energy field a special shortcoming has been encountered in that chromates and dichromates decompose rather rapidly under intense nuclear irradiation, such that ferrous metal is soon left unprotected to the corrosive ravages of the aqueous solutions. Of late, this special shortcoming has proven particularly acute in the case of nuclear reactors utilizing aqueous solutions of uranium, or other fissionable material, as the chain-fission-reactive fuel. Typically, one such nuclear reactor comprises an aqueous solution of uranyl sulfate approximating 0.1 molar circulated, under superatmospheric pressure and elevated temperature (ca. 1,000 p. s. i. and 250° C.), through a spherical stainless steel tank (to wit: Number 347 stainless steel) wherein a sufficient quantity of the solution is continuously amassed to maintain a self-sustaining chain fission reaction. For further details as to the construction and operation of such a reactor, reference may be made to copending applications of the common assignee, as: S. N. 355,262, filed May 15, 1953, in the names of C. B. Graham and I. Spiewak, for “Improved Neutronic Reactor Control Method and System”; S. N. 321,078, filed November 18, 1952, in the names of C. E. Winters et al., for “Improved Neutronic Reactor Operational Method and Core System.”

During operation, corrosion of the stainless steel tank by the aqueous uranyl sulfate is especially treacherous in this case, since the corrosive action decreases the acidity, leading to the progressive precipitation of uranium oxides, which represents hazardous accumulation of fissionable material as a highly-concentrated precipitate. Such accumulation of exothermic-fission-reacting material would soon produce a localized “hot spot,” serving to weaken the pressure vessel or other apparatus in the immediate proximity, along with inducing strong convection currents, possibly boiling, and other adverse thermal effects, and even more seriously could ultimately result in a hapless run-away chain fission reaction. Consequently, for continued successful operation of the reactor, unchecked corrosion of such vessels is altogether intolerable. The severe corrosive action of so strong a salt solution as 0.1 molar uranyl sulfate, and the pronounced acceleration imparted by the 250° C. elevated temperature, do not simplify the problem. In the past, it had become the

practice to afford temporary protection to the vessels by pre-treating the apparatus with hot aqueous chromic acid—e. g., by circulating ca. 2% chromic acid through the apparatus at 250° C. for from 4 to 24 hours. While such pre-treatment seems to prevent rather thoroughly any significant oxidation of the ferrous metal at the outset of subsequent reactor operation, the protection tends to deteriorate under prolonged intense irradiation, as evidenced by progressively more pronounced uranium precipitation, making periodic repetition of the pre-treatment necessary to maintain effective protection. The duration of even this temporary protection afforded by chromic acid pre-treatment is not adequately dependable; while draining the uranium solution from the reactor tank system and pretreating as becomes necessary—say at intervals of a few weeks—has been acceptable practice for experimental reactor operation at low power, the same would drastically detract from efficiency when applied to practical-power-producing nuclear reactor operations.

Consequently, there has been an increasing desire that better methods be found for mitigating and curbing corrosion of ferrous metal by aqueous solutions, especially one affording dependable protection under exposure to intense nuclear irradiation, particularly in the environs of the chain-fission-reactive core of a nuclear reactor.

Accordingly, one object of the present invention is to provide an improved method for inhibiting corrosion of ferrous metals by aqueous solutions.

Another object is to provide such a method which is simply effected by the incorporation of a small amount of an inhibitory agent into the aqueous solution.

A further object is to provide such a method which affords at least equivalent inhibition with substantially smaller amounts of reagent than necessary in the case of previously-conventional inhibitory agents.

Still another object is to provide such a method which is operable at elevated temperatures, especially temperatures above 100° C. and on up through the order of 250° C.

Still a further object is to provide such a method wherein the essential inhibitory reagent is of superior stability for withstanding intense nuclear irradiation, and wherein inhibitory effectiveness is retained through extended periods of exposure in the proximity of a chain-fission-reacting amassment.

Still another object is to provide such a method which is of appropriate fitness and suitability for practical chemical-processing and atomic-energy applications.

Additional objects will become apparent hereinafter.

In accordance with the present invention, a new and improved method for inhibiting corrosion of ferrous metal by an aqueous solution comprises providing a small concentration, greater than a trace concentration, or technetium, in the form of pertechnetate ion, dissolved in said solution. Applicant has discovered that the pertechnetate ion, when incorporated and maintained in aqueous solutions in contact with ferrous metal apparatus, is generally capable of thoroughly preventing rusting or other visible corrosion of the metal, or detectable weight loss by the metal; it is effective in this manner when applied to such mild conditions as plain water at room temperature on up through such harsh conditions as aqueous strong electrolytes in low concentrations at 250° C. Applicant has further discovered that for this, much smaller amounts of pertechnetate ion are needed than are required of chromate ion for similar protection; for at least equivalent inhibition, the pertechnetate ion concentration required is at so different a level that at least one order of magnitude lower than that of chromate ion has been found sufficient. Moreover, it has been found that the aqueous pertechnetate ion is eminently stable with respect to intense nuclear irradiation. Upon direct exposure to operating nuclear reactor irradiation, aqueous millimolar KTcO_4 solutions, both alone and containing uranyl sul-

fate (with uranium component isotopically enriched to 93% U-235 , to afford exposure of pertechnetate immediately within a fissioning aqueous solution), no decomposition or reduction was manifested throughout irradiation wherein the solutions accumulated a total of so much as ca. 3×10^{21} electron volts of energy absorbed per milliliter of solution. Pertechnetate also proved itself to be stable under intense gamma-ray irradiation; upon several minutes irradiation in a 1000-curie cobalt-60 source, similar aqueous potassium pertechnetate solutions remained stable in the presence of air under the resulting bombardment with gamma radiation. Also, pertechnetate solutions in such use appear to retain their inhibitory effectiveness indefinitely. For example, a sample of carbon-steel has been immersed for over a year in an aqueous solution of potassium pertechnetate of concentration equivalent to 50 parts per million technetium, and even though the system has been continuously exposed to air and maintained at temperatures varying between 100° C. and room temperature, the metal still retains a bright, clear surface and has experienced no detectable weight loss; under substantially identical conditions, but in the absence of technetium, a similar sample showed rust within a few minutes and was thoroughly encrusted with rust in a few weeks. Similarly, an immersed sample of carbon-steel in an aqueous solution containing 10 parts per million of chloride ion (as KCl) together with potassium pertechnetate equivalent to 50 parts per million of technetium, has retained a clear, shiny surface and has sustained no significant weight loss for over a year, although under identical circumstances but with the absence of technetium a similar sample showed rust after 10 minutes, and lost almost 10% of its weight through corrosion within a period of three months. Being of such efficiency, and having such beneficial attributes, the present method clearly affords substantial practical advantages for general protection of ferrous metal from aqueous corrosion.

Aside from the aforementioned advantages concerning concentration sufficiency and radiation stability, applicant has found more fundamentally that the pertechnetate ion is rather unique among reagents of its type generally, in emulating the chromate ion and thus in affording any practical corrosion inhibition at all. That is, attempts to achieve like inhibition with perrhenate ion, perruthenate ion, vanadate ion, and molybdate ion, have revealed that none of these is an effective inhibitor; while some formation of reaction films was observed in all of the above cases, nevertheless the same proved ineffective, for severe pitting and corrosion occurred without apparent abatement. It is appreciated that strength of oxidizing potential alone is no criterion for ability to inhibit such corrosion effectively; it is noteworthy that in the case of the perruthenate ion, which has the strongest oxidation potential of the several reagents mentioned, corrosion was found to proceed unimpeded and actually to be worse than in the absence of perruthenate ion. Nor is similarity of chemical nature determinative of inhibition efficacy; significantly, rhenium is in the same sub-group (group VII-A) in the periodic table with technetium, indeed is the next heavier element in that sub-group immediately below technetium, and forms a singly negatively charged tetroxide anion (perrhenate) precisely paralleling the pertechnetate ion, but yet perrhenate concentrations on up to complete saturation were found to permit corrosion to proceed steadily and without evident restraint. However, among all of these agents tried, the pertechnetate ion, specifically, proved to be an outstanding exception, in that it has the essential ability—reminiscent of the chromate ion—to stifle recurrent outbreaks of corrosion at their very incipience, wherein protection of the metal surface is continuously repaired and re-established such that a dynamic continuing inhibition is realized. Too, corrosion already underway is likewise arrested.

In conducting the present invention, the constitution of metal-plus-solution systems which admit of effective application of the instant inhibition method are subject to wide variation. Applicability extends over the range of corrodible ferrous metals, ranging from cast iron and machine steel, on through carbon-steel and electrolytic iron and up to and including the corrosion-resistant ferrous alloys, such as the stainless steels. Naturally, it is desirable that the aqueous corroding solution to which this pertechnetate method is applied should not contain serious amounts of other agents which would serve to reduce, precipitate, complex, or otherwise effectively destroy or remove pertechnetate ions from aqueous solution. Representative of the legion of corrosive aqueous media, encountered in practice, which satisfy these requirements are, along with pure water, brines as well as other alkali, and ammonium, chloride solutions and other aqueous inorganic salt solutions from millimolar concentrations up to saturation, aqueous mineral acids, such as H_2SO_4 , of acidity so great as pH of 1 and greater, inorganic bases such as aqueous alkali, and the like.

Upon encountering such a system, corrosion is inhibited in accordance with the present invention simply by initially dissolving a soluble source of pertechnetate ion into the aqueous solution. The pertechnetate ion—i. e., TcO_4^- —is the singly charged tetroxide anion of the highest valence state of technetium, the artificial element of atomic number 43. Although artificial, technetium is currently being produced in usable quantities as a product of nuclear fission; in conventional practice, technetium is found—consistently in only trace concentrations—in spent aqueous reactor fuel solutions and solutions of dissolved spent solid reactor fuel elements undergoing chemical reprocessing, whereupon it is readily separated and isolated as a by-product of nuclear reactor operation. Availability, preparation, and chemistry of technetium and its compounds are known in the art. In this connection reference may be made to papers of: G. E. Boyd, et al., *Journal of the American Chemical Society*, vol. 74, page 556–557, 1952; J. W. Cobble et al., *Journal of the American Chemical Society*, vol. 74, page 1852, 1952; and G. W. Parker et al., "Isolation of Milligram Amounts of Element-43 from Uranium Fission," Doc. #AECD-2043, available from U. S. Atomic Energy Commission, Technical Information Division, Oak Ridge Operations, Oak Ridge, Tennessee.

Being highly soluble, and possessing a normally-innocuous cation, potassium pertechnetate is the particularly preferred source of the inhibitory anion, although other soluble pertechnetate salts, e. g., $NaTcO_4$ and NH_4TcO_4 are likewise satisfactory. Although the pertechnetate may be dissolved into the corrosive solution in solid salt form, its addition in the form of a standardized aqueous solution proves more convenient in practice.

Concerning the amount of pertechnetate ion required, it has been experienced that a concentration of technetium greater than a trace concentration is required in the corroding aqueous solution for effective inhibition. For matter of definition, it is to be understood that the term "trace" is used herein in its quantitative sense to denote concentrations of less than 5 micrograms per gram of total solution medium, in accordance with its accepted meaning in the art as defined in Hack's *Chemical Dictionary*, third edition, edited by J. Grant, page 863, published by the Blakiston Co., Philadelphia. Above this minimum concentration level, it becomes appropriate to use progressively greater pertechnetate concentrations commensurate with the harshness of the corrosive nature of the aqueous solutions encountered. Typical of the pertechnetate concentrations indicated to be appropriate for virtually complete curtailment of corrosion (i. e., no visible rust; no detectable weight loss) under varying degrees of corrosive nature indicated, are outlined in Table I below.

TABLE I

Typical pertechnetate ion concentrations appropriate for effective corrosion inhibition

System	Approximate minimal pertechnetate ion concentration
Carbon steel in:	
Distilled water.....	5×10^{-6} M
Demineralized water to 250° C.....	5×10^{-6} M
Tap water.....	$2.5 \text{--} 5 \times 10^{-4}$ M
Water +10 p. p. m. Cl^- to 100° C.....	5×10^{-4} M
Water +10 p. p. m. Cl^- to 250° C.....	$1 \text{--} 2 \times 10^{-3}$ M
Electrolytic iron in: Water +10 p. p. m. Cl^-	5×10^{-5} M
Stainless steel (Number 347) in:	
Water +2 p. p. m. Cl^- to 250° C.....	$1 \text{--} 5 \times 10^{-4}$ M
0.1 M UO_2SO_4 to 250° C.....	$1 \text{--} 5 \times 10^{-3}$ M
0.1 N H_2SO_4 +10 p. p. m. Cl^- at 100° C.....	1×10^{-4} M

Where the volume of aqueous solution is not particularly small with respect to the area of ferrous metal in contact therewith and the metal surfaces are not seriously abraded, the proportion of technetium content actually expended to provide the inhibition is normally insignificant, such that the inhibitory effect of the pertechnetate concentration originally established in the solution will ordinarily be retained indefinitely. However, in the presence of reductants or other agencies which tend adversely to destroy or remove the pertechnetate concentration from the solution, it may be necessary to replenish the pertechnetate ion concentration periodically in order to afford continued protection. A most desirable situation is that where the aqueous corroding solution, in the form of a stream, is passed quickly through the ferrous metal apparatus to be protected, in which case the pertechnetate ion is incorporated to an appropriate concentration in the aqueous stream prior to its entry into the ferrous metal apparatus, such that the pertechnetate ion concentration of solution in contact with the metal would hardly have opportunity to become insufficient. Importantly, along this line, a ferrous metal surface protected by pertechnetate in the instant manner normally loses its protection almost immediately upon removal of the pertechnetate, consequently making it necessary that all subsequent replacement solutions should also have pertechnetate established therein to an appropriate concentration.

For particular application to the service of inhibiting ferrous metal corrosion by an aqueous fractional-molar uranyl sulfate fuel solution of a nuclear reactor, the pertechnetate ion has shown itself to be beneficial not only in indefinitely retaining its stability and inhibitory effectiveness in the presence of such strong electrolyte when heated up to 250° C. and when subjected to sustained reactor irradiation to cumulative dosages of the order of 10^{20} to 10^{21} e. v./cc., but as an additional incidental advantage the pertechnetate ion has proved to increase substantially the temperature at which such an aqueous uranyl sulfate solution adversely separates into two liquid phases. In more detail, it is known that the uranyl sulfate-water system enters a two-liquid-phase region at temperatures above 200° C. depending upon the concentration of uranyl sulfate present [cf. C. H. Secoy, "System of Uranyl Sulfate-Water — Temperature-Concentration Relationships Above 250° C.," *Journal of the American Chemical Society*, vol. 72, page 3343 (1950)]; while the temperature for the separation of two-liquid-phases in the case of uranyl sulfate equivalent to 40 grams of uranium per liter approximates 300° C., it was found that the presence of ca. 0.1 molar potassium pertechnetate resulted in displacement of the temperature for such phase separation to 322° C. This should profitably afford considerable revision upward of the maximum practicable operational temperatures of uranyl-sulfate-solution-fuelled nuclear reactors. Otherwise, the compatibility of lower

pertechnetate concentrations with aqueous uranyl sulfate has also been confirmed.

The texture of the ferrous metal surface affects greatly the propensity toward corrosion, and in turn the extent of the role played by the pertechnetate inhibitor. Rough, abraded surfaces tend to corrode much more rapidly than polished surfaces; likewise, upon applying pertechnetate inhibition, the amount of technetium that remains upon the uncorroded metal after it is removed from the corrosive aqueous solution, washed, and dried is similarly highly dependent upon the condition of the surface of the metal. Since technetium is radioactive, the amounts thereof deposited upon the surface in the course of corrosion inhibition may readily be assessed by radiation determination instruments, and the distribution of the technetium across the surfaces delineated through the preparation of autoradiograms. Typically, under otherwise identical conditions, an electropolished ferrous metal specimen seems to pick up only about $\frac{1}{4000}$ as much technetium as an abraded surface. For example, it was found that with Number 347 stainless steel specimens immersed in aqueous sulfuric acid of pH 0.9, containing ten parts per million chloride ion (as KCl) together with 1×10^{-4} M KTCO_4 , at $85^\circ\text{--}100^\circ\text{C}$. for 2 hours, a specimen which had been hand-polished with 2/0 abrasive paper bore 95,000 counts per minute per square centimeter of technetium radioactivity, while an electropolished specimen bore only 120 counts per minute per square centimeter. (Note: 2×10^7 counts per minute with the same counting technique correspond to 1 milligram of technetium in a very thin film.) Further, corresponding to the well-known fact that the activity of a metal in corrosion may be increased in areas subjected to stress or to mechanical work, it was found that technetium seeks out such areas having enhanced activity. With carbon steel discs, the faces of which had been polished after machining, autoradiograms showed a light and rather uniform coating on the faces with heavy exposure on the rims. Similarly, in the case of a piece of Number 347 stainless steel sheet which was cut, partly abraded, and deliberately scratched with a file in places, an autoradiogram showed the traces of the scratches to be clearly defined, whereas the areas that were least abraded manifested almost no technetium deposition. Evidently such deposition of technetium as occurs, parallels chemical attack upon the metal. In the same vein, investigation has revealed that unpolished weld surfaces and adjacent area are especially active, being anodic to polished or machine surfaces in the proximity; autoradiograms of Number 347 stainless steel which had been exposed to aqueous corrosion in the presence of pertechnetate ion disclosed clearly the contours of the weld zone in both a fusion weld and a weld made with filler rod. Too, when a specimen Number 347 stainless steel bar was electropolished on three sides and ground on the fourth, the ground surface picked up 80% of the technetium activity, although it had only 25% of the total geometrical surface.

It is thought that the mechanism of corrosion inhibition here likely is principally one involving adsorption of pertechnetate ion upon the metal surface, rather than reduction of TcO_4^- to TgO_2 to engage in the formation of an oxide film. First of all, it has been experienced that upon removing carbon steel from an aqueous solution containing pertechnetate ion wherein substantially complete corrosion inhibition had been realized, the metal corroded almost immediately when subsequently exposed either to moist atmosphere or to water containing no pertechnetate ion; the rapidity of loss of protection from the metal surface tends to rule out an adherent oxide film as the protective agency. Furthermore, upon immersing a carbon steel specimen as an electrode in the cathode compartment of a three-compartment diaphragm primary electrolytic cell (with cellophane diaphragms and employing a zinc anode) with the electrolyte being potassium sulfate

of 0.05 to 0.10 molar and the electrodes were connected through a microammeter it was found that when the solution in the catholyte compartment was replaced by aqueous potassium sulfate of the same concentration but containing 0.001 molar KTCO_4 , the cell current dropped by 30 to 45%; when the pertechnetate solution was next withdrawn and replaced by aqueous potassium sulfate alone, the current quickly returned to its original value. During the electrolysis, a visible blue-bronze coloration was formed upon the carbon-steel cathode; this discoloration remained after the removal of the pertechnetate solution but did not prevent the current from returning to its initial value, seeming to lend weight to the proposition that the diminution of cathodic current was due to adsorbed technetium, rather than to an oxide film which might be represented by the blue-bronze coloration. Similar results were obtained in which copper was used as the second electrode, wherein the carbon steel specimen became the anode. Moreover, it has been found possible to attain substantially complete inhibition of the corrosion of carbon steel in water with potassium pertechnetate wherein only about 20 counts per minute per square centimeter of technetium radioactivity is found after the exposure of the metal to the aqueous solution, although it would take ca. 3400 counts/min./cm.² to correspond to a monomolecular film of deposited technetium dioxide; this is deemed indicative that the inhibition is not the result of a continuous film of a reduced technetium oxide or other precipitated technetium reaction product. Also, it was found, for instance, that upon immersion of carbon-steel in distilled water containing ca. 10 parts per million chloride ion together with a pertechnetate ion concentration approximating 50 parts per million technetium maintained alternately hot and cold for seven weeks, a specimen of carbon-steel progressively accumulated a technetium deposit over the first three hours of immersion, which then generally stabilized at about 38,900 counts per minute of technetium radioactivity and thereafter remained nearly constant for seven weeks until the end of the observation, having a terminal activity of about 37,000 counts per minute; this seems to indicate that the function of technetium is not one of forming scar film to repair an iron oxide protective film, since there is no continual progressive build-up of technetium activity. Rather, when considered together with the rapid loss of protection upon removal of technetium from the solution, this is suggestive of a dynamic absorption effect with continuous equilibrium exchange of pertechnetate between a state of attachment to active sites on the metal surface and a state of ionization in the aqueous solution. However, it is not intended that this invention be limited to any particular theory concerning the nature of the mechanism involved.

Further illustration of the quantitative aspects and preferred reagents and procedures of the present method is provided in the following specific examples. In Example I, a series of orienting experiments qualitatively indicate the effectiveness of different concentrations of pertechnetate ion in inhibiting corrosion, and compare the same with chromate ion.

EXAMPLE I

Individual drops of various aqueous media, including tap water, tap water having potassium pertechnetate or potassium chromate dissolved therein, in some cases including a concentration of chloride ion as well, were placed at separate locations upon the upper horizontal surfaces of plates of pure electrolytic iron and of carbon steel. The plates were exposed to air and the drops were permitted to evaporate to dryness at room temperature. Thereupon, the spot where each drop had been was visually inspected for manifestation of corrosion. Observations are tabulated in Table II below.

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TABLE II

Natural evaporation of aqueous media from metal plates

PART A

[Metal: Electrolytic iron.]

Aqueous medium	Results
Tap water.....	Heavy rust spot.
K ₂ TcO ₄ (0.01 M).....	Clean surface.
Equivalent mixture of tap water 0.01 M K ₂ TcO ₄ (K ₂ TcO ₄ =0.005 M).....	Do.
K ₂ CrO ₄	Do.

PART B

[Metal: Carbon steel (SAE 1010).]

Aqueous medium	Results
Tap water.....	Severely rusted.
Tap water +K ₂ CrO ₄ (K ₂ CrO ₄ =0.003 M).....	No rust; slightly yellow.
Tap water +K ₂ TcO ₄ (K ₂ TcO ₄ =0.003 M).....	Clear surface.

PART C

[Metal: Electrolytic iron. Aqueous Media: Tap water +Cl⁻ (ca. 10 p. p. m. as KCl)+inhibitory agent.]

Inhibitory agent	Results
5×10 ⁻⁵ M K ₂ TcO ₄	Clear.
4×10 ⁻⁵ M K ₂ TcO ₄	Clear (1 speck rust).
2.5×10 ⁻⁵ M K ₂ TcO ₄	Do.
1×10 ⁻⁵ M K ₂ TcO ₄	Partly rusted.
5×10 ⁻⁴ M K ₂ CrO ₄	Clear.
4×10 ⁻⁴ M K ₂ CrO ₄	Clear (1 speck rust).
2.5×10 ⁻⁴ M K ₂ CrO ₄	Do.
1×10 ⁻⁴ M K ₂ CrO ₄	Partly rusted.

The results in foregoing Table II illustrate the effectiveness of the pertechnetate ion in inhibition. A full order of magnitude difference between the low concentrations of pertechnetate ion sufficient for service and the high chromate ion concentration required, and the unblemished protection afforded by K₂TcO₄ down to concentrations of five parts per million (i. e., 5×10⁻⁵ molar) clearly appear. In Example II, following, the continued effectiveness through periods approaching one year duration are demonstrated.

EXAMPLE II

PART A

Two 1 x 2 centimeter strips of carbon steel (SAE 1010) were hand-polished with 2/0 abrasive paper, and each immersed in a different aqueous medium in respective test tubes. The medium in which the first strip was immersed was distilled water containing no pertechnetate, while the second strip was immersed in distilled water containing pertechnetate ion equivalent to 50 parts per million technetium (i. e., 5×10⁻⁴ M K₂TcO₄). The test tubes were loosely stoppered to permit access of air, and were maintained at 100° C. during the day (ca. 8 hours; 5 days per week) and were permitted to cool to room temperature overnight. The volume of each aqueous medium was maintained at a reasonably constant 10 milliliters throughout the experiment by periodic replenishment with fresh distilled water to replace that evaporated. From time to time the metal strips were carefully removed from the tubes, dried by gentle rubbing between paper towels to remove any loosely-adherent corrosion products, and weighed to a precision of ±0.1 mg. The observed weights are tabulated in Table III below.

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PART B

The same procedure as in part A above was employed, with the exception that each aqueous medium also contained 10 parts per million chloride ion, as KCl. Results are reported in Table III below.

TABLE III

Corrosion inhibition with pertechnetate continuing for periods approaching one year

PART A

Date	Weights of metal strips	
	No TcO ₄ ⁻	With TcO ₄ ⁻
January 7 (initial).....	.5613 grams (Spotted with rust in 10 minutes).	.6245 grams (metal clear).
January 21.....	.5563.....	.6245.
February 5.....	.5569.....	.6244.
March 17.....	.5420.....	.6244.
March 31.....	.5404 (discarded).....	.6243 (not heated after April 7).
October 2.....		.6244.
January 8 (next year).....		.6244 (metal still clear) (solution water-white).

PART B

Date	Weights of metal strips	
	No TcO ₄ ⁻	With TcO ₄ ⁻
January 15 (initial).....	.5698 (Spotted with rust in 10 minutes).	.5728 (metal clear).
January 22.....	.5650.....	.5728.
January 30.....	.5585.....	.5725 (5). ¹
February 16.....	.5472.....	.5726.
March 17.....	.5336 (discarded).....	.5727 (not heated after April 7).
October 2.....		.5727 (metal still clear) (solution water-white).

¹ Sample dropped in sink.

Example III further extends to demonstration of efficacy of pertechnetate inhibition to temperatures so high as 250° C.

EXAMPLE III

A number of substantially identical carbon steel specimens, hand-polished with 2/0 abrasive paper were each mounted by wedging one edge into a respective tetrafluoroethylene polymer ("Teflon") block. Each disc so mounted was individually disposed in a stationary platinum-lined bomb of ca. 50 cc. internal volume. A 10 cc. portion of a different aqueous medium, as indicated, was added to the bomb with each respective disc, whereupon in each case the bomb, with the remainder of its interior filled with cold air, was sealed and disposed in a salt bath thermostated at 250° C. After a duration in the salt bath, as indicated, the bomb in each case was removed from the salt bath, opened, the contents visually examined, and the disc removed from the block, dried by rubbing between paper towels, and weighed. The visual observations, and a comparison of the weights of each disc before and after the exposure in the bomb, are tabulated in

Table IV below.

TABLE IV

Inhibition of corrosion of carbon steel at 250° C.

Aqueous medium	Water ¹	Water ¹ + TeO ₄ ⁻ (=10 p. p. m. Te)	Water ¹ + TeO ₄ ⁻ (=5 p. p. m. Te)	Water ¹ + TeO ₄ ⁻ (=100 p. p. m. Te)	Water ¹ +10 p. p. m. Cl ⁻	Water ¹ +10 p. p. m. Cl ⁻ + TeO ₄ ⁻ (=2×10 ⁻³ M TeO ₄ ⁻)
Duration of exposure	92 hrs.	116 hrs.	116 hrs.	92 hrs.	1 hr.	1 hr.
Weights of disc:						
Initial	0.2828	0.2911	0.2748	0.2870	(ca. ¼ gm.)	(ca. ¼ gm.)
Final	0.2738 ²	0.2911	0.2747(5)	0.2870	(lost 0.8 mg.)	No change ± 0.1 mg.
Appearance of disc	Rusted	Iridescent film (no rust)	Iridescent film (no rust)	Iridescent film (no rust)	Extensive corrosion	Blue-bronze film (no rust)
Appearance of solution	Rusty	Water-clear	Water-clear	Water-clear	Red-brown corrosion product (muddy liquid)	Water-clear

¹ Demineralized water.² Incompletely descaled.

Effectiveness in application to stainless steel at 250° C. is revealed qualitatively in Example IV.

EXAMPLE IV

Each of a pair of one square centimeter strips of 10-mil-thick No. 347 stainless steel sheet were heated while immersed in respective bodies of aqueous media, following the block-mounting and platinum-lined-bomb technique as employed in Example III. In both cases the aqueous solutions comprised principally demineralized water containing 2 parts per million of chloride ion (as KCl); one solution, however, contained potassium pertechnetate equivalent to 40 parts per million technetium, while the second contained no pertechnetate ion. This test lasted, in both cases, 234 hours at 250° C. At the conclusion of the test, the metal strip in the solution containing pertechnetate showed only an adherent bronze-blue color; on the other hand, rusty red areas were apparent upon the surfaces of the strip which had been immersed in the solution containing no pertechnetate. A radiation count of the strip which had been immersed in the pertechnetate solution indicated ca. 1000 counts/min./cm.² of technetium radioactivity.

Experiment V, following, demonstrates the efficacy of the instant inhibition method when applied to a situation of aqueous concentration, temperature, and metal identity approximately those encountered in aqueous-solution-fuelled nuclear reactors.

EXAMPLE V

Each of a pair of half-inch-long pins of ¼₁₆ inch diameter Number 347 stainless steel rod were disposed in a respective loosely-fitting fused silica tube, together with uranyl sulfate solution equivalent to 300 grams uranium per liter filling the remainder of the tube. The aqueous solution in the first tube contained no pertechnetate ion, while that in the second tube was 4×10⁻³ molar in KTcO₄. The tubes were largely de-aerated by alternate freezing and thawing of the solutions under reduced pressure, whereupon the tubes were sealed. The tubes were slowly rotated end-over-end in an oven, and were opened after the following heating period: 14 hours at 250° C., 32 hours at 235° C., and 44 hours at room temperature. The pin which has been exposed to solution containing no pertechnetate showed much red-brown scale and sediment; the pin was easily rubbed down to bright metal with a paper towel, and the ends of the pin were already bright from striking the ends of the silica tube. In the tube containing pertechnetate, there was no brown sediment; the pin was lightly coated—sides and ends—with a black film that could not be removed by mild rubbing with a paper towel (possibly attributable to presence of silicic acid in solution dissolved from the tube). Analysis gave a strong test of iron in the solution containing no pertechnetate, but only a faint trace in the pertechnetate

sample. Initial weight of each pin, and its final weight after removal from the tube and drying by rubbing with a paper towel, along with observations through the silica tubes during the course of the heating, are tabulated in Table V below.

TABLE V

Inhibition of corrosion of stainless steel by uranyl sulfate solution at 250° C.

	Tube	
	Without TeO ₄ ⁻	With TeO ₄ ⁻
Weight of pin:		
Initial	0.1413	0.1488
Final	0.1403	0.1487 (5).
Observation of tube contents during heating:		
After 14 hours	Pin darkened.	Pin shiny black; turbidity ¹ in solution.
After 46 hours	Pin dark+red precipitate.	Do.
After 90 hours	do.	Do.

¹ Presumably silica.

Example VI, following, illustrates the criticality of maintaining the technetium concentration greater than a trace concentration (i. e., 5 parts per million technetium or greater) in the interest of thorough protection.

EXAMPLE VI

Employing generally the same procedure as in Example II, five 1 x 2 cm. strips of SAE 1010 carbon steel were hand-polished with 2/0 abrasive paper, whereupon each was immersed in a 10 milliliter portion of distilled water in the bottom of respective test tubes. The first tube contained no pertechnetate dissolved in the water, while the remaining tubes contained potassium pertechnetate dissolved therein equivalent to 3, 5, 7, and 10 parts per million technetium respectively. The tubes were loosely stoppered to admit access of air, were maintained at 100° C. during the day, and were permitted to cool to room temperature overnight. Aqueous volume in each case was retained reasonably constant at 10 milliliters by periodic replenishment with fresh distilled water to replace that evaporated. The condition of the strips was visually observed from time to time, and, after a suitable period in each case, each strip was removed from the tube, dried gently between paper towels to remove any corrosion products, and weighed. The determined weights and visual observations are tabulated in Table VI below.

At the close of these operations, the solution in the tube containing 10 parts per million technetium was made 10 parts per million in dissolved chloride ion (as KCl); it was observed that the sample commenced to corrode, showing local rust spots within about an hour at 100° C.

TABLE VI

Corrosion inhibition with minimal concentrations of pertechnetate

	Water ¹	Water 1+TeO ₄ ⁻ (=3 p. p. m. Te)	Water 1+TeO ₄ ⁻ (=5 p. p. m. Te)	Water 1+TeO ₄ ⁻ (=7 p. p. m. Te)	Water 1+TeO ₄ ⁻ (=10 p. p. m. Te)
Weight of strip:					
Initial.....	0.5714	0.5872	0.5581	0.5535	0.5577.
End of 6 days.....	0.5691				
End of 2 weeks.....		0.5817	0.5580	0.5535	0.5577.
Visual observations:					
After 8 mins.....		2 spots rust.....			
After 2 hrs. 25 mins.....		Local rust ulcers.....			
After 6 hrs. 45 mins.....		Local corrosion; solution turbid.		Metal bright; solution clear.	
After 6 days.....	Considerable loose rust; pits.		Metal bright; solution clear.		Metal bright; solution clear.
After 2 weeks.....		Extensive rust areas.	Metal bright; solution clear.	Metal bright; solution clear.	

¹ Distilled water.

While this invention has been described with particular emphasis upon its application to the inhibition of ferrous metal corrosion in, specifically, aqueous-solution-fuelled nuclear reactors, it is inherently of much wider applicability. The present method is well adapted to inhibiting corrosion, in a similar fashion, under difficult conditions of intense nuclear irradiation arising in the technical processing of radioactive aqueous solutions, such as spent reactor fuel solutions; aqueous reactor fuel solutions become radioactive as a consequence of the formation of radioactive fission products therein during fission operation, which solutions must customarily be reprocessed periodically for recovery of the remaining fissionable material therein and decontamination of the same from fission products. Furthermore, the present method has broad applicability in chemical processing operation wherein no significant radioactivity whatever is involved. Various additional applications of the hereinbefore disclosed method will become apparent to those skilled in the art. It is, therefore, to be understood that all matters contained in the above description and examples are illustrative only and do not limit the scope of the present invention.

What is claimed is:

1. A new and improved method of inhibiting corrosion of a ferrous metal by an aqueous medium in contact therewith, which comprises providing, throughout the entire period of contact of said medium with said metal, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said medium.

2. The method of claim 1 wherein said pertechnetate ion is provided in the form of alkali pertechnetate.

3. The method of claim 1 wherein said pertechnetate ion is provided in the form of potassium pertechnetate.

4. The method of claim 1 wherein said ferrous metal is carbon steel.

5. The method of claim 1 wherein said ferrous metal is electrolytic iron.

6. The method of claim 1 wherein said ferrous metal is a nickel-chrome stainless steel.

7. A new and improved method of inhibiting corrosion of a ferrous metal by an aqueous medium at elevated temperatures up to approximately 250° C., which comprises providing, throughout the entire period of contact of said medium with said metal, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said medium.

8. A new and improved method of inhibiting corrosion of a ferrous metal by an aqueous medium in contact therewith under conditions of substantial nuclear irradiation, which comprises providing, throughout the entire period of contact of said medium with said metal, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said medium.

9. A new and improved method of inhibiting corrosion of a ferrous metal by an aqueous medium in contact therewith under conditions of substantial nuclear radiation emanated from a self-sustaining chain-fission reaction, which comprises providing, throughout the entire period of contact of said medium with said metal, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said medium.

10. A new and improved method of inhibiting corrosion of carbon steel by an aqueous potassium chloride solution equivalent to 10 parts/million of chloride ion in contact therewith at elevated temperatures up to approximately 100° C., which comprises providing, throughout the entire period of contact of said medium with said metal, a concentration of approximately 50×10^{-5} molar pertechnetate ion dissolved in said medium.

11. A new and improved method of inhibiting corrosion of nickel-chrome stainless steel by an aqueous uranyl sulfate solution in contact therewith, which comprises providing, throughout the entire period of contact of said solution with said steel, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said solution.

12. A new and improved method of inhibiting corrosion of a nickel-chrome stainless steel by an aqueous uranyl sulfate solution in contact therewith under conditions of substantial nuclear radiation emanated from a self-sustaining chain-fission reaction, which comprises providing, throughout the entire period of contact of said solution with said metal, a concentration of at least approximately 5×10^{-5} molar pertechnetate ion dissolved in said solution.

References Cited in the file of this patent

- U. S. Atomic Energy Commission AECD-3065, Sept. 19, 1945, High-Power Water Boiler, available from Technical Information Service, Oak Ridge, Tenn., pages 1 and 2.
G. W. Parker et al.: AECD-2043, pages 1-3.
Scientific American, April 1950, pages 41 and 43.