

[54] METHOD FOR PROTECTION OF
EVAPORATOR HEATING ELEMENTS
FROM CORROSION

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[57] ABSTRACT

The corrosion of heating elements in evaporators for alkaline media is substantially prevented by using chromium steel containing preferably 25–28 percent chromium as the metal for the heating elements in the presence of 0.05 to 1g/l of sodium chlorate.

4 Claims, No Drawings

METHOD FOR PROTECTION OF EVAPORATOR HEATING ELEMENTS FROM CORROSION

This invention relates to methods for corrosion protection of heating elements in evaporators operating in alkaline media, for example, in evaporators used for the manufacture of caustic soda. The aforesaid evaporators are intended for carrying out the processes of concentrating (evaporating) alkaline solutions under elevated temperatures and diverse service conditions, such as natural or forced circulation of alkaline solutions, various pressures of heat carrier (heating steam), erosion due to the circulation of alkaline pulp containing a significant proportion of solid matter, etc.

During the service life of evaporating plant equipment the principal elements of evaporators, viz., heating tubes, undergo maximum deterioration under the effect of corrosive alkaline media and also suffer from pronounced erosion corrosion, particularly where evaporator operation involves forced circulation of alkaline solutions containing different admixtures.

Diversified methods for corrosion protection of heating elements of evaporators intended for handling alkaline media are known in the art.

For example, use is made of heating elements manufactured from corrosion-resisting materials, e.g. nickel, nickel-base alloys, or high-alloy austenitic steels which contain, apart from chromium, molybdenum and other alloying elements, also an adequately high proportion of nickel, viz. 25–28 percent.

In some instances recourse is had to equipment made from ordinary steel, provided diverse inhibitors, such as sodium nitrate or saccharose, are incorporated into the alkaline corrosive medium.

It is further known to effect corrosion protection by the anode polarization technique.

The known methods for corrosion protection suffer from the drawback of resorting to heating elements made from nickel, which is a critical metal, or from nickel-base alloy and nickel-bearing steels, the employment of nickel for this purpose being particularly undesirable in view of the constantly growing consumption of nickel for the production of heat-resistant and high-temperature alloys. This situation has prompted world-wide studies directed to the development of steels and alloys containing a lower percentage of nickel and to finding conditions, under which steels containing little or no nickel would exhibit corrosion-resisting properties for specific applications.

The aforesaid studies are essentially aimed at minimizing the consumption of nickel for the equipment to be used in large-tonnage manufacturing processes, among which mention may be made of caustic soda production, under temperature conditions which do not necessarily heat-resistant materials.

The known methods involving the use of corrosion inhibitors are not invariably effective, particularly where the equipment to be protected is made from carbon steel.

The employment of anodic protection in heating elements is likewise inefficient due to the principles on which the design of these elements is based.

It is an object of the present invention to eliminate the aforesaid disadvantages.

It is a further and more specific object of the present invention to provide a method for corrosion protection of heating elements of evaporators handling alkaline media which will make it possible to improve substantially the dependability and service life of heating elements and to make the heating elements from non-critical materials.

According to the invention, the objects have been accomplished by the provision of heating elements made from chromium steels which undergo passivation under the effect of an inhibitor, sodium chlorate, present in a concentration of 0.05–1 g/l in an alkaline medium at a temperature of 90–450° C.

A protective film formed as a result of the interaction between chromium steel and a chlorate-containing alkaline solution exhibits high adhesiveness to the base metal and is

also noted for its good resistance to erosive effects caused by a rapid stream of hot alkaline medium (stream rate, 4–5 m/sec) containing about 20 percent of solid phase, e.g. sodium chloride in the manufacture of caustic soda.

No incorporation of the corrosion inhibitor (sodium chlorate) in alkaline solution is required when manufacturing caustic soda, since in this case sodium chlorate is the by-product of caustic soda manufacture and is present in the alkaline solution in an amount of 0.05–1 g/l which is adequate for chromium steel passivation.

Where no sodium chlorate is present in alkaline solution, the aforespecified amount of the inhibitor should be incorporated into the solution being handled.

Currently available equipment manufactured from chromium-nickel steel containing 18% Cr and 10% Ni can be used in conjunction with the heating elements, according to the present invention, since the contact between the aforesaid steel and chromium steel (25% Cr) is permissible and a heating element may be assembled by flaring chromium steel tubes in a tube sheet made from chromium-nickel steel.

It is also preferable to use chromium steel or carbon steel clad with chromium steel for fabricating tube sheets of heating elements.

Data listed in Table 1 pertains to laboratory experiments under static conditions in a 50 percent solution of sodium hydroxide and made it possible to evaluate the behavior of various steel grades and of nickel in an alkaline environment at temperatures that are close to those used for the evaporation of alkaline solution under plant conditions.

Table 1
Corrosion rate, mm/year

Metal	Content of sodium chlorate, g/l	Temperature, °C		
		100	120	140
Carbon steel	0.0	0.62	1.90	3.70
	1.0	2.8	5.1	7.9
Steel containing 18% Cr and 10% Ni	0.0	0.20	0.31	0.71
	1.0	0.44	1.20	1.90
Steel containing 18% Cr, 12% Ni and 3% Mo	0.0	0.16	0.20	0.54
	1.0	0.32	0.82	1.4
Steel containing 25% Cr	0.0	0.18	0.28	2.1
	1.0	0.021	0.08	0.08
Nickel (99.5% Ni)	0.0	0.08–0.1	0.08–0.1	0.08–0.1
	1.0	0.08–0.1	0.08–0.1	0.08–0.1

It follows from the above data that among the steels tested chromium steel is unique in that it exhibits high corrosion resistance in corrosive alkaline medium throughout the range of test temperatures.

Under the same conditions, carbon and chromium-nickel steels undergo dissolution at a high rate and the presence of an oxidizing component (sodium chlorate) exerts a marked accelerating effect on the rate of corrosion.

Hence, carbon steel and also chromium-nickel steel and chromium-nickel-molybdenum steel at elevated temperatures are devoid of corrosion resistance.

Chromium steel is noted for its high corrosion resistance under the conditions specified hereinbefore and is not inferior to nickel, a scarce metal, in this respect.

Similar results confirming high corrosion resistance of chromium steel containing 25–28 percent of chromium were obtained under conditions of caustic soda melting in the presence of sodium chlorate as an inhibitor, whereby the sodium hydroxide content grew from 44–45 to 96 percent.

Steel grade	Starting specimen weight, g.	Sodium chlorate content g/l	Table 2	
			Temp. °C	Specimen weight loss during test period, 180 hrs, in grams.

Steel containing 25-28% Cr	8.3476	0.0	340-350	4.3209
- " "	8.2192	0.0	340-350	4.7269
- " "	8.3326	1.0	340-350	0.2214
- " "	9.6231	1.0	340-350	0.2026

It is apparent from the data of Table 2 that even at high temperatures the inhibiting action of sodium chlorate is retained, the rate of the specimen corrosion in melted alkali in the presence of sodium chlorate being 20-23 times lower than without sodium chlorate.

With reference to chromium steels containing a lower percentage of chromium (13 and 17% Cr), it is evident that these materials retain an adequate corrosion resistance and undergo passivation in a 30 percent solution of sodium hydroxide containing sodium chlorate.

Table 3 summarizes the results of laboratory tests on chromium steel specimens containing 13 and 17% Cr. Corrosion resistance was evaluated at different temperatures in a 30 percent solution of sodium hydroxide containing sodium chlorate.

Steel grade	Content of sodium chlorate, g/l	Table 3 Corrosion rate, mm/year			
		Temperature, °C			
		100	120	140	160
		0.6	1.3-1.8	-	-
Steel containing 13% Cr	0.35-0.45	0.19	0.77	-	-
Steel containing 17% Cr	0.0	0.24	0.45	0.60	-
	0.35-0.45	0.07	0.08	0.15-0.20	0.68

It is apparent from the data of Table 3 that increasing the degree of alloying the steel with chromium results in broadening the range of temperatures at which this type of steel retains its ability to undergo passivation in a 30 percent solution of sodium hydroxide.

For a better understanding of the present invention, presented hereinbelow are the following examples of plant tests on specimens of diverse metals placed in the tubes of heating elements in evaporators at caustic soda plants. Tests were also conducted on tubes made from appropriate metals and flared in the tube sheets of heating elements in evaporators used for evaporating electrolytic caustic soda from diaphragm cells.

EXAMPLE 1

Plant tests were conducted on specimens made from diverse steel grades, viz., chromium-nickel steel containing 18% Cr and 10% Ni; chromium-nickel-molybdenum steel containing 18% Cr, 12% Ni and 3% Mo; and chromium steel containing 17% and 25% Cr, in a medium consisting of 42 percent solution of sodium hydroxide, in which the content of sodium

chlorate equals 0.8-1 g/l and the content of sodium chloride equals 20 g/l, the temperature of the heating steam being 120° C.

Apart from the corrosive action exerted by the medium, the test specimens undergo erosion caused by a high-speed stream of alkaline pulp (V stream = 4-5 m/sec)

Under the aforespecified conditions, the steel specimens are corroded at the following rate, millimeters per year:

Steel containing 18% Cr and 10% Ni	2.5
Steel containing 18% Cr, 12% Ni, and 3% Mo	1.8
Steel containing 25% Cr	0.06
Steel containing 17% Cr	1.2

EXAMPLE 2

Plant tests were conducted on tubes made from carbon steel, chromium-nickel steel containing 18% Cr and 10% Ni, chromium-nickel-molybdenum steel containing 18% Cr, 12% Ni and 3% Mo, and chromium steel containing 25% Cr, test conditions being identical to those disclosed in Example 1.

The tubes made from the aforesaid materials were found to have the following service life, months:

carbon steel tubes	2 to 3
chromium-nickel and chromium-nickel - molybdenum steel tubes	6 to 8

In the tubes made from chromium steel, continuous service resulted in neither corrosion damage of the tubes nor diminution of the tube wall thickness. At the sites of flaring the tubes in the tube sheets of heating elements there developed no leaks.

The present method is useful not only for corrosion protection of evaporator heating elements, but also for corrosion protection of equipment handling alkaline media under the aforesaid conditions in diverse chemical processes.

What we claim is:

1. In a method of dehydrating an aqueous alkaline solution by evaporating water from said solution at a temperature of 90° to 450° C. while in contact with metal surfaces, the improvement which comprises adding 0.05 to 1g/l of sodium chlorate to the alkaline solution and utilizing a metal consisting of chromium steel containing 25 to 28 percent of chromium.

2. In a method of dehydrating an aqueous alkaline solution containing chlorate ions by evaporating water from said solution at a temperature of 90° to 450° C. while in contact with metal surfaces, the improvement which comprises utilizing a metal consisting of chromium steel containing 25 to 28 percent chromium.

3. A method according to claim 1 wherein the aqueous alkaline solution is an aqueous solution of sodium hydroxide.

4. A method according to claim 2 wherein the aqueous alkaline solution is an aqueous solution of sodium hydroxide and sodium chloride.

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