Stress Corrosion Cracking of Corrosion Resistant Alloys in Halide Brines Exposed to Acidic Production Gas

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Introduction

A program partly sponsored by the American Petroleum Institute (API) studying the interaction of completion brines and corrosion-resistant alloys (CRAs) has been underway for several years. An earlier paper [1] addressed the effect of thiocyanate (SCN^-) corrosion inhibitor on promoting stress corrosion cracking (SCC) in CRAs exposed to halide brines, with a link to field failures. The current paper addresses SCC risks upon exposure of brines to an ingress of acidic production gas (CO_2 or CO_2 + H_2S) or to air, both of which, have resulted in field failures. Test protocols are presented. Brine severity is related to halide ion concentration, including formation of complex ions with. Testing focused on a group of 13Cr martensitic stainless steels alloyed with Ni and Mo, with more limited tests of duplex stainless steels (SS) and high-Ni alloys. SCC results are presented in relation to alloy resistance and to test variables, including temperature, pH, and additives to the brine.

Stress Corrosion Cracking of Corrosion Resistant Alloys in Halide Brines Exposed to Acidic Production Gas

1 Scope

The annular space between the production tubing and the carbon steel casing is filled with a dense fluid, typically a halide salt. In wells with corrosion resistant alloy (CRA) tubing, SCC of the CRA tubing OD or auxiliary components has occurred in a number of wells. Halide brines have densities up to 2.2 g/ml (19.2 lb/gal or ppg) and contain a number of additives. A previous publication linked some field failures to the addition of SCN-corrosion inhibitor. [1]

Additional field failures in $CaCl_2$ brines have been linked to ingress of acidic gas containing CO_2 and H_2S and to exposure to air. SCC of martensitic stainless steel (SS), (13 % Cr, 6 % Ni, 2 % Mo) was attributed to downhole leakage of acidic gas [2], whereas SCC of a duplex SS tubing (25 % Cr, 3 % Mo) was attributed to air in the gas cap above column of brine. [3]

To understand the effects of brine compositions on the CRAs, a joint industry project was formed under the auspices of the American Petroleum Institute (API). It has been known as the CRAs in Brine Testing Program. Under its auspices, work has been underway for a number of years on understanding the interaction of brine chemistry and CRAs.

The current paper evaluates the SCC risks of a range of CRAs in various halide brine compositions for the case of exposure to acidic production gas (CO_2+H_2S). Also evaluated are SCC risks due to air exposure. However, the testing became focused on a group of martensitic stainless steels alloyed with Ni and Mo, that are collectively referred to as modified 13Cr martensitic SS, or alternatively in some publications as super (S13Cr) martensitic SSs. Most tests evaluated the as-received brine, excluding proprietary additives such as corrosion inhibitor or oxygen scavengers. For completeness and comparison, test results provided by member companies in the API program or in the publications are cited; these test protocols may be different from those in the API test protocols hence, where that occurs, significant differences are noted.

2 Abbreviations and Symbols

2.1 Abbreviations

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
AYS	actual yield stress
BS	bar stock
CRA	corrosion-resistant alloys
HRC	hardness Rockwell cone
JIP	joint industry project
ksi	1000 pounds-force per square inch
MSS	martensitic stainless steel
MTR	material test report
NACE	National Association of Corrosion Engineers
OD	outside diameter
PEEK	polyetheretherketone
PTFE	polytretrafluoroethylene
ppg	pounds per gallon

psi	pound-force per square inch
SCC	stress corrosion cracking
SCE	saturated calomel electrode
SEM	scanning electron microscopy
SS	stainless steel
SPE	Society of Petroleum Engineers
S13Cr	super 13 % chromium
UNS	unified numbering system
UTS	ultimate tensile strength
YS	yield stress
13Cr	13 % chromium
@RT	at room temperature
@T	at temperature

2.2 Symbols

BrO_3^-	bromate ion
$CaBr_2$	calcium bromide
$CaCl_2$	calcium chloride
CaO	calcium oxide
CO_2	carbon dioxide
$Ca(OH)_2$	calcium hydroxide
C276	chromium-nickel molybdenum alloy
H_2S	hydrogen sulfide
HSO_3^-	hydrosulfite (bisulfite) ion
M	molar concentration, expressed in moles per liter
NaBr	sodium bromide
Na_2CO_3	sodium carbonate (soda ash)
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
Nb	niobium
N_2	nitrogen
O_2	oxygen
P_{CO2}	carbon dioxide pressure, expressed in pounds-force per square inch (psi).
P_{H2S}	carbon dioxide pressure, expressed in pounds-force per square inch (psi).
SCN	thiocyanate
$ZnBr_2$	zinc bromide

3 Experimental Procedures

3.1 General

The test results from the current API program follow a detailed protocol, outlined in Table 1.

Table 1—API Test Protocols in Autoclave Testing in Halide Brines

C-ring preparation	C-rings were cut from tubular with mill scale removed or machined from bar stock.
Loading	C-rings were loaded to yield strength (YS) following NACE TM0177-2005 method C [4]. YS was obtained by mill certificate or calculated by derating to test temperature.
Creviced C-rings	In some high-Ni tests a strip of C-276 was spot-welded on the C-ring apex to form a crevice.
Electrical isolation	C-ring isolation from the C-276 loading bolt used a PEEK insulating washer. Isolation was measured prior to and after testing. Tests where isolation was not maintained and with a crack, were rejected.
Brine preparation	Commercial grade brines were used, with a chemical analysis provided. Component brines were stirred before blending.
Autoclave testing	Testing was performed in a four liter C-276 autoclave, with 20 % volume head space. Each test contained up to eight C-rings, individually isolated from each other and the autoclave wall.
Buffer addition	When noted in text, Na_2CO_3 was added to NaBr, $Ca(OH)_2$ or CaO to $CaBr_2$. $CaBr_2$ brines were filtered before use.
Brine pH	pH was measured without dilution using procedures described in SPE 86502 with a double junction reference electrode, at room temperature, before and after testing.
Tests with O_2	Brine was purged with either air (3 psi O_2) or a N_2–O_2 mixture at room temperature.
De-aeration	After sealing, three vacuum evacuation cycles with N_2 were performed. De-aerated brine was transferred, then a final N_2 purge was made.
Other additives in some tests	When noted, (1) erythorbate or HSO_3^- O_2 scavenger or (2) a filming amine corrosion inhibitor for carbon steel casing was added.
Tests with CO_2	Transfer of de-aerated brine was followed by a CO_2 purge for two or more hours. After heating to test temperature, CO_2 purge was added to reach target pressure.
Tests with CO_2+H_2S	Transfer of de-aerated brine was followed by a purge of a H_2S/CO_2 gas mixture for two hours, and then locked in at ambient pressure. The autoclave was then heated to the target temperature. The autoclave was then increased in pressure with either CO_2 or H_2S/CO_2 depending on the environment. Draeger tubes were utilized to ensure target H_2S was obtained. Adjustments were performed for the first day, day three, and on a weekly basis if needed.
Test failure	Cross sectioning was often required. A crack designation was assigned if crack-like features were greater than 25 μm.
Exposure time	SCC resistance is based on 30-day tests. The 14-day tests explored test variables. Some 90-day tests are included.

Stress reduction at 265 °F was about 7.5 % from that at room temperature and was approximately 11 % for tests performed at 350 °F.

The API protocol of total saturation of CO_2 at P_{CO2} may represent a more severe test than gas leakage under field conditions. The latter case would correspond to absorption of a volume of CO_2 in the annular column of brine that represents gas leakage [5, 6] rather than full saturation.

The U.S. customary unit (USC) system is used in this Technical Report. Factors hereafter permit conversions of USC units to standard international (SI) units or SI-derived units.