NACE INTERNATIONAL

THE CORROSION SOCIETY

Sulfur-Related Corrosion Mechanisms

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October 8th, 2010
Calgary, AB

DOWNHOLE CORROSION IN SOUR GAS ENVIRONMENTS

Aggressive environment due to H_2S, CO_2, Cl^- and high T & P

Environment:

Sour Gas (H_2S, CO_2, CH_4)
Brine (100,000 ppm+ Cl^-)
↑ T (200°C - 250°C)
↑ P (20,000 psi)

Sulfur ($f(x_{H2S}, T, P)$)

↓

1) Weight loss corrosion
2) Localized or pitting attack
3) Stress corrosion cracking (SCC)

Presence of Elemental Sulfur Increases Severity of the Environment

CRA APPLICATIONS IN SOUR GAS ENVIRONMENTS

Alloy	User	Location	Product	
2205	Tenneco	Gulf of Mexico	Tubing	High Cr stainless
2205	Tenneco	Gulf of Mexico	Liner	
2205	Shell	Gulf of Mexico	Tubing	
2205	ARCO	Gulf of Mexico	Liner	
2205	Chevron	Tuscaloosa	Tubing	
DP-3	ARCO	Gulf of Mexico	Liner	
S-28	Shell	Southwest Texas	Tubing	
S-28	ARCO	Gulf of Mexico	Tubing	
S-28	Exxon	Big Escambia, Ala.	Tubing	
825	O.I.L.	Arbuckle, Okla.	Liner	Ni-base CRA
825	Shell	Miocene, Tex.	Tubing	
825	Mesa	Gulf of Mexico	Tubing	
825	Gulf	Gulf of Mexico	Tubing	
2550	Hunt	Smackover, Miss.	Liner	
2550	Exxon	La Barge, Wyo.	Tubing	
G-3	Shell	Southwest Texas	Tubing	
G-3	Shell	Miocene, Tex.	Tubing	
C-276	Shell	Southwest Texas	Casing	
C-276	Exxon	Smackover, Miss.	Casing	
C-276	Mobil	Mobile Bay, Ala.	Liner	

2205: Fe - 5.5 Ni - 22 Cr - 3 Mo - 0.14 N
DP-3: Fe - 6 Ni - 25 Cr - 1.5 Mo - 0.1 N
S-28: Fe - 31 Ni - 27 Cr - 3.5 Mo - 1 Cu
825: Fe - 42 Ni - 22 Cr - 3 Mo - 2.25 Cu
2550: Fe - 50 Ni - 25 Cr - 6 Mo

Source: Craig, B.D., et al., Careful Planning Improves CRA Selection for Corrosive Elements, Pet. Eng. Int., pp. 26-30, July, 1992.

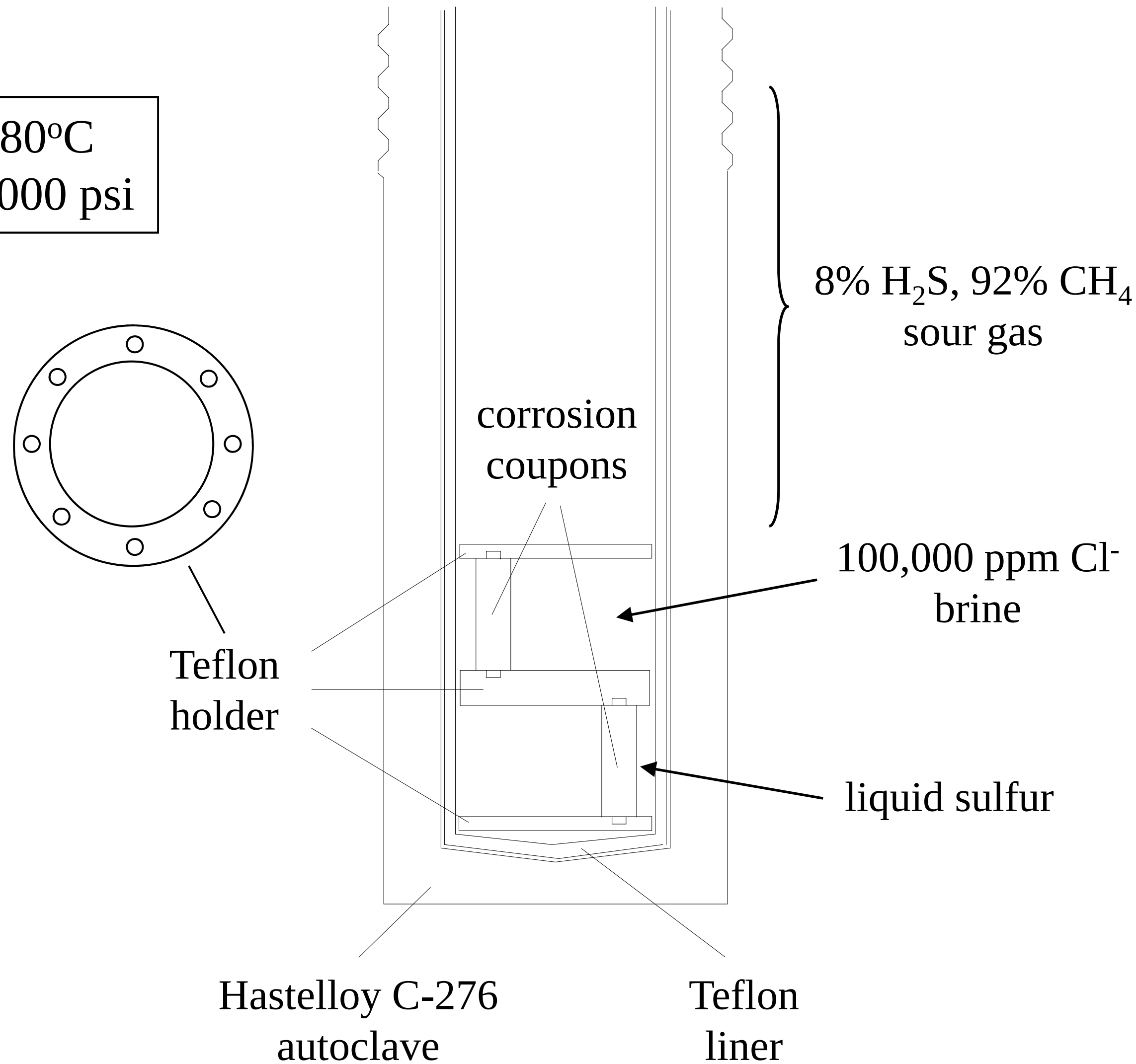
TEST MATERIALS

Composition, wt % (~balance Fe)

		Cr	Ni	Mo
Ni – Base CRA	Haselloy C-276	15	56	16
	Carpenter 625+	21	61	8
	Hatelloy G-50	22	45	9
	NKK NIC-42-110 (825)	21	42	3
Stainless	SS 316	16-18	10-14	2-3
Sour Rated HSLA	Cr/Mo	1	---	0.2-0.6
	Mn Alloy		(Mn 1.3%)	

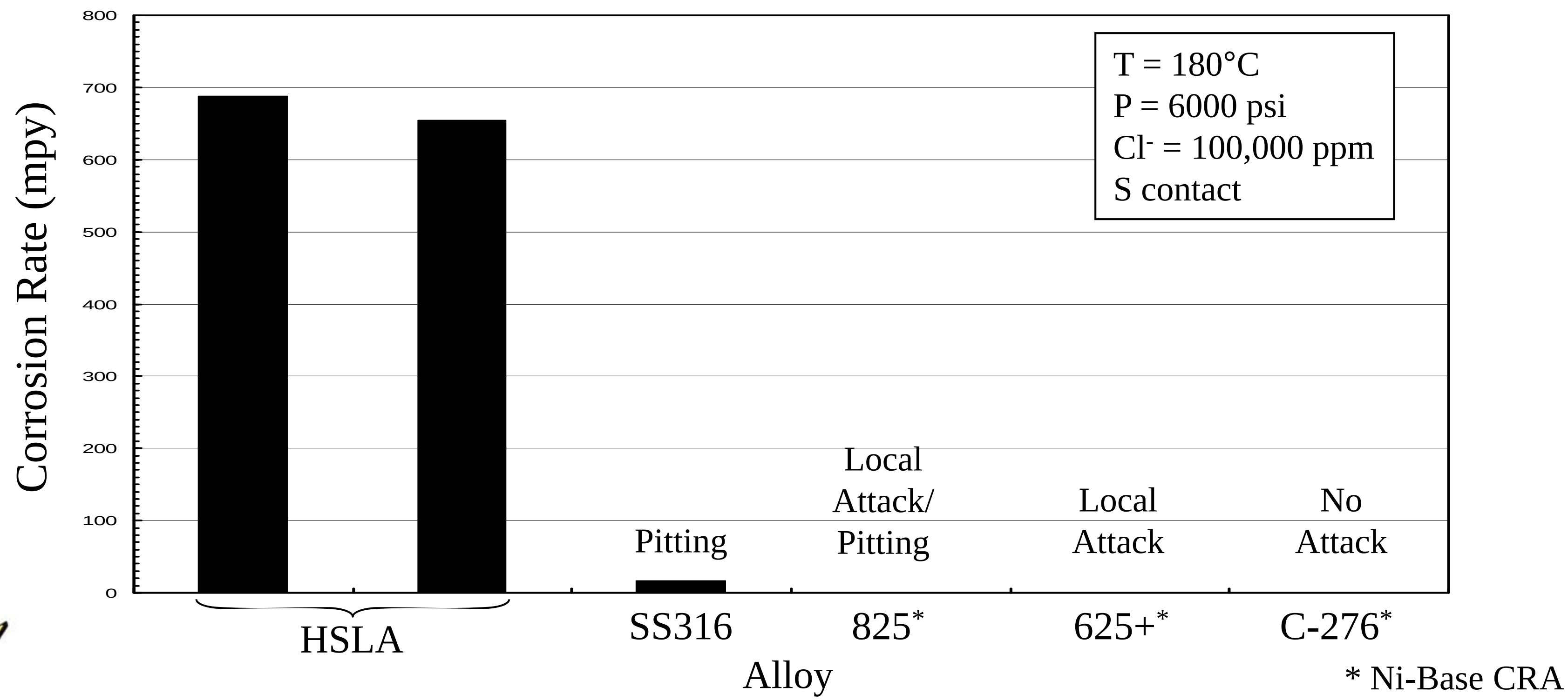
SCHEMATIC OF AUTOCLAVE SETUP FOR DOWNHOLE CORROSION TESTS

T = 180^{o}C
P = 6000 psi



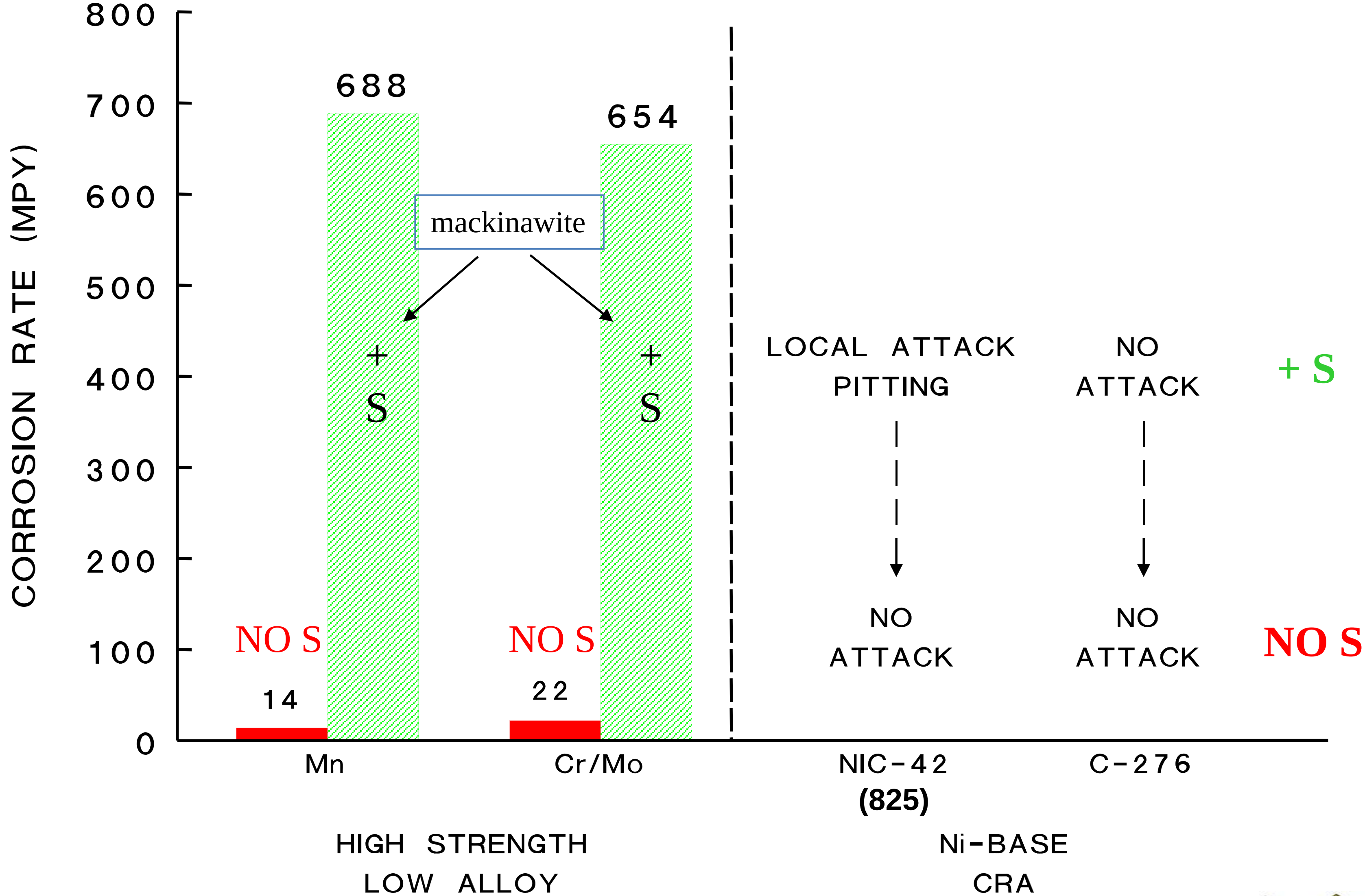
CORROSION OF SELECTED ALLOYS IN A 8%H_2S/92%CH_4 SULFUR/BRINE ENVIRONMENT AT 180ºC

Uncorroded Mn Cr/Mo SS316 825 625+ C-276



CORROSION OF HIGH AND LOW ALLOYS IN A SOUR GAS / BRINE ENVIRONMENT IN THE PRESENCE AND ABSENCE OF ELEMENTAL SULFUR

(8% H_2S, 92% CH_4 ; 180°C ; 6000 psi ; 100,000 ppm Cl^- ; 14 day exposure)



STRESS CORROSION CRACKING OF CRA MATERIALS IN A SOUR GAS / BRINE ENVIRONMENT IN THE PRESENCE AND ABSENCE OF ELEMENTAL SULFUR

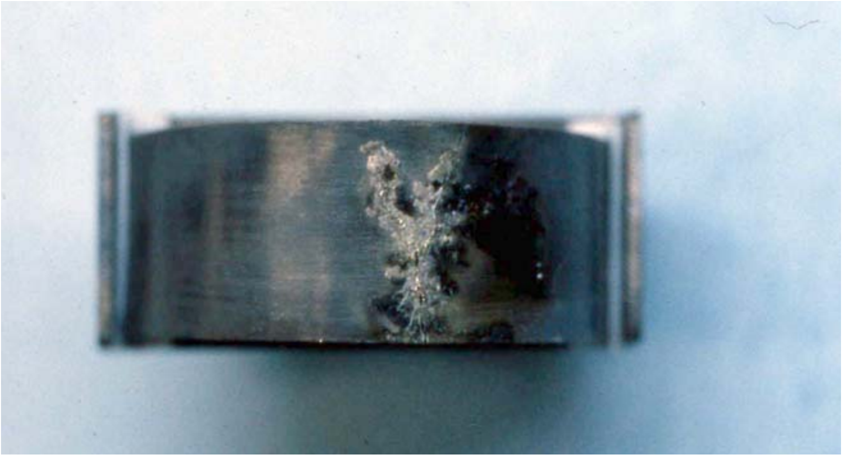
(8% H_2S, 92% CH_4 ; 200°C ; 6500 psi ; 100,000 ppm Cl^- ; 14 day exposure)

% Composition		Hastelloy C-276	Carpenter 625+	Hastelloy G-50	Nippon Kokan NIC-42 (825)	Stainless 316
	Ni	57	61	45	42	10-14
	Cr	16	21	22	22	16-18
	Mo	16	8	9	3	2-3

Corrosion Environment	Hastelloy C-276	Carpenter 625+	Hastelloy G-50	Nippon Kokan NIC-42 (825)	Stainless 316
'no sulfur'	NC	NC	NC	NC	CRACKED
'added S_8' (2 g/l in brine) - NO DIRECT CONTACT	NC	NC	NC	CRACKED	FAILED
'added S_8' (70% sub-saturated sour gas) - NO DIRECT CONTACT	NC	NC	NC	CRACKED (less severe)	CRACKED/ FAILED
'added S_8' (free-standing S phase) - DIRECT CONTACT	NC	NC	NC	*NC*	FAILED

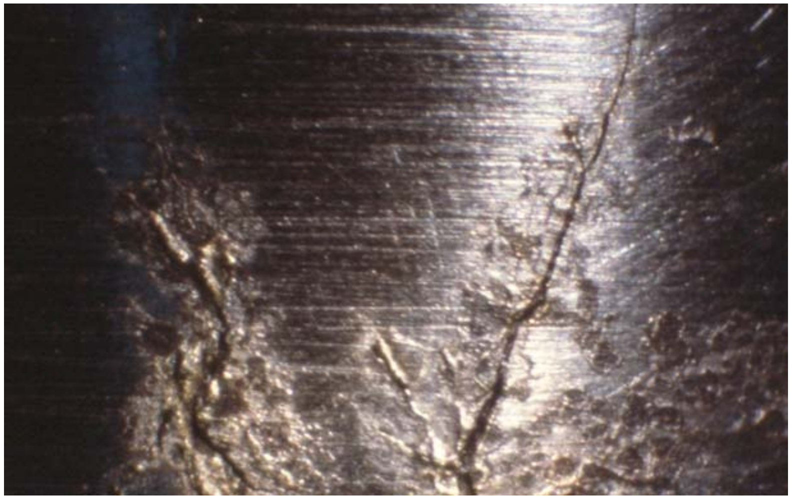
NC = NO CRACKING

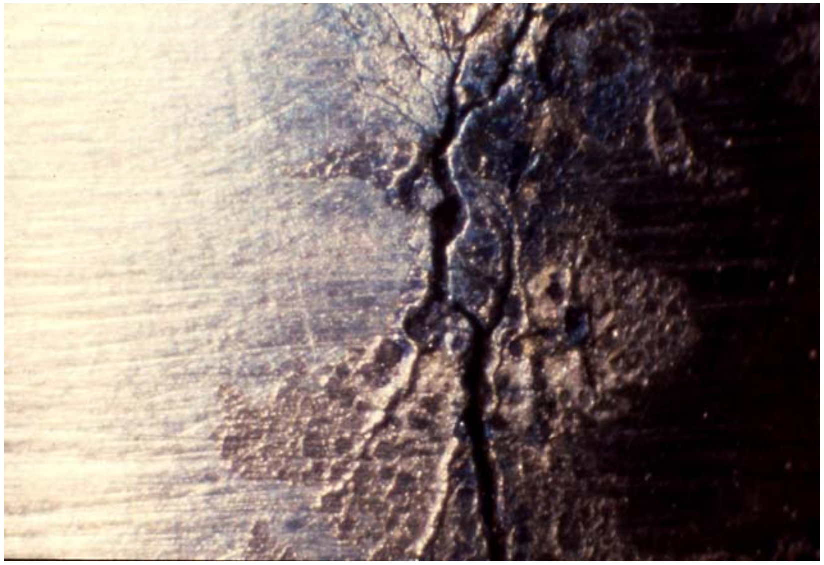
SULFUR PROMOTED CRACKING OF ALLOY 825 UNDER DOWNHOLE CONDITIONS AT 200ºC



2 g/L sulfur
added to brine

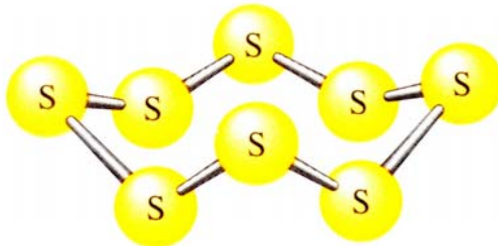
'no contact' with
free-standing S phase



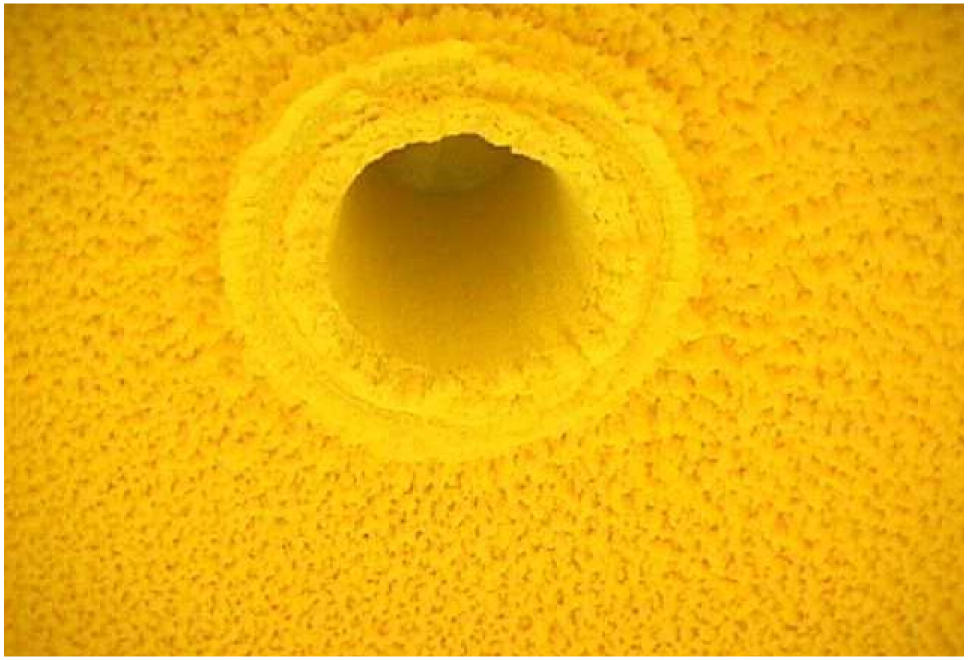


No cracking w/o S

TWO EXAMPLES OF SULFUR DEPOSITION IN SOUR GAS FACILITIES



S_8 deposition within a sour gas flow line[+]

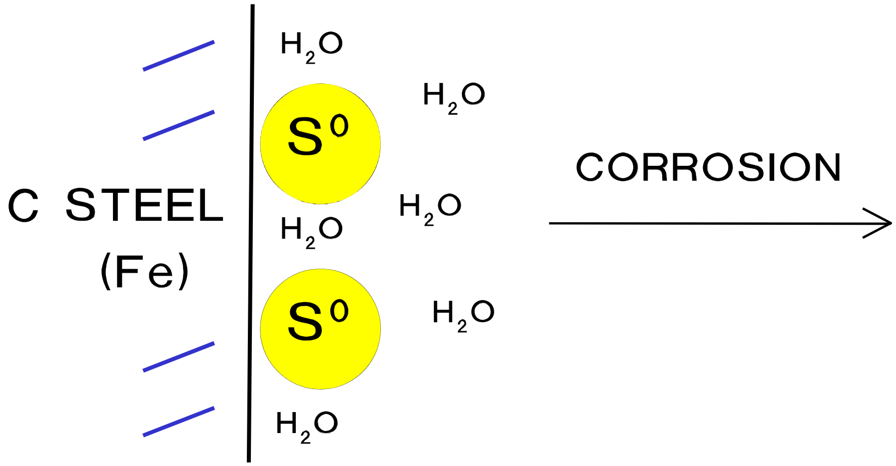


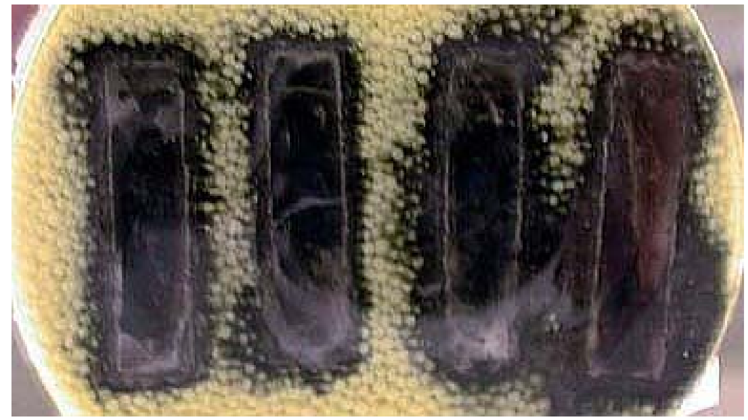
S_8 deposition in a gas plant inlet separator*

[+] Photograph courtesy of John Morgan, John M. Campbell & Company

* Photograph courtesy of Mark Townsend, Burlington Resources

ELEMENTAL SULFUR (CONTACT) CORROSION





$$Fe^{0} + S^{0} \longrightarrow \overset{(2+)(2-)}{FeS}$$

CR: 60 – 500 mpy

ACID CORROSION HYPOTHESIS

$$4S + 4H_2O \longrightarrow H_2SO_4 + 3H_2S$$

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

DIRECT SULFUR CORROSION

$$Fe + S \longrightarrow FeS$$

S^0 ACTS DIRECTLY AS THE CORRODENT

ELECTROCHEMICAL MECHANISM OF SULFUR CORROSION

Anodic: $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathodic: $S + 2e^- \xrightarrow{[FeS]} S^{2-}$

Overall Corrosion Reaction: $Fe + S \xrightarrow[H_2O]{[FeS]} FeS$

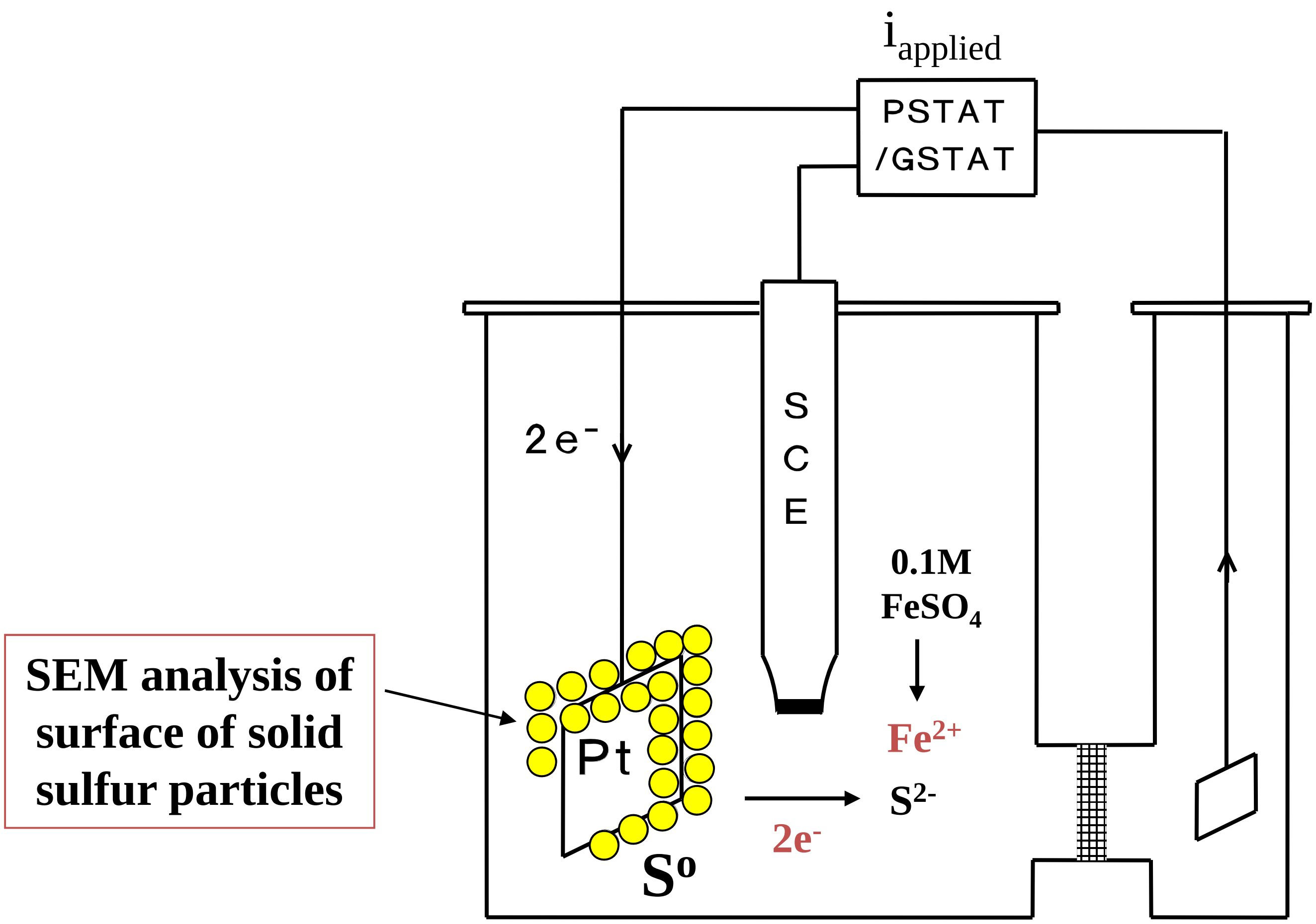
STEEL SULPHUR IRON SULPHIDE

"MACKINAWITE"

S-deficient $FeS_{(1-x)}$
"non-stoichiometric"

NO CONTACT, NO CORROSION

ELECTROCHEMICAL STUDY OF REDUCTION OF SOLID ELEMENTAL SULFUR

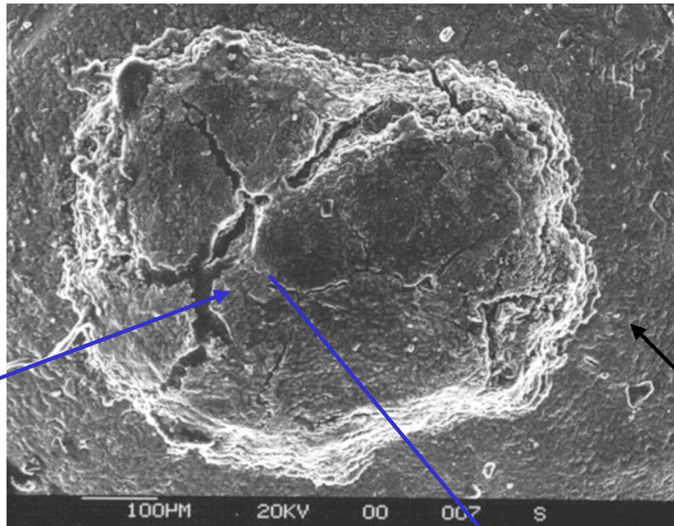


$$S^0 + 2e^- \xrightarrow{Fe^{2+}} FeS$$

Fe^{2+} added to solution + provide $2e^-$

SEM ANALYSIS OF DIRECT ELECTROCHEMICAL REDUCTION OF SOLID SULFUR

FeS layer formed by reduction of sulfur

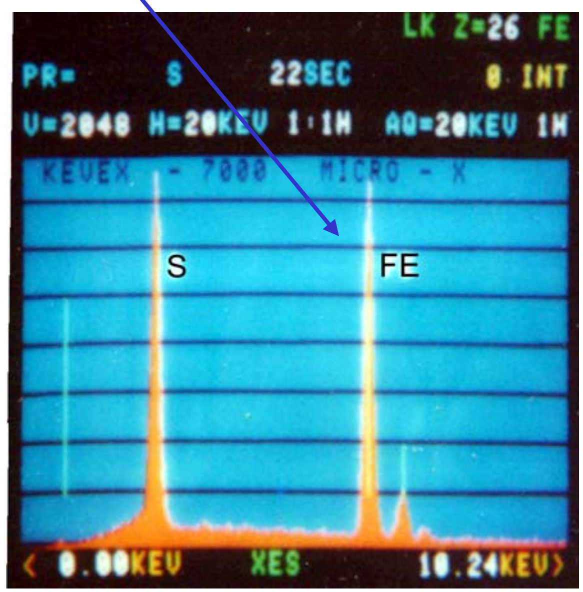


FeS

S^0

Electrochemical reduction: $S^0 + 2e^- \xrightarrow{Fe^{2+}} FeS$

XES analysis of FeS layer



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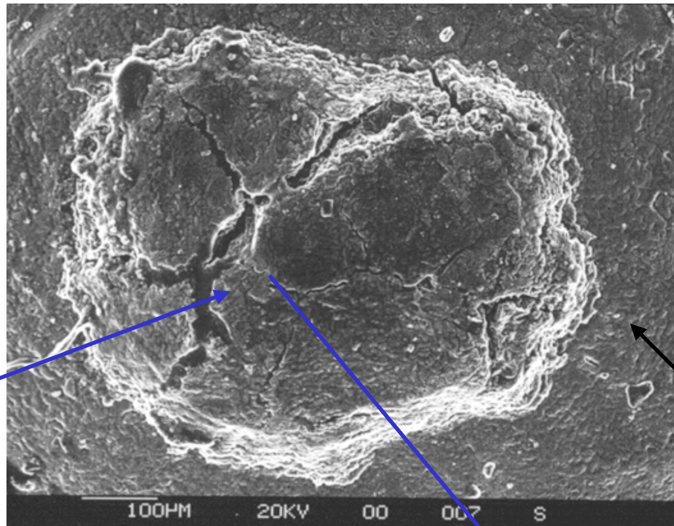
SEM ANALYSIS OF DIRECT ELECTROCHEMICAL REDUCTION OF SOLID SULFUR

FeS layer formed by reduction of sulfur



FeS

S^0

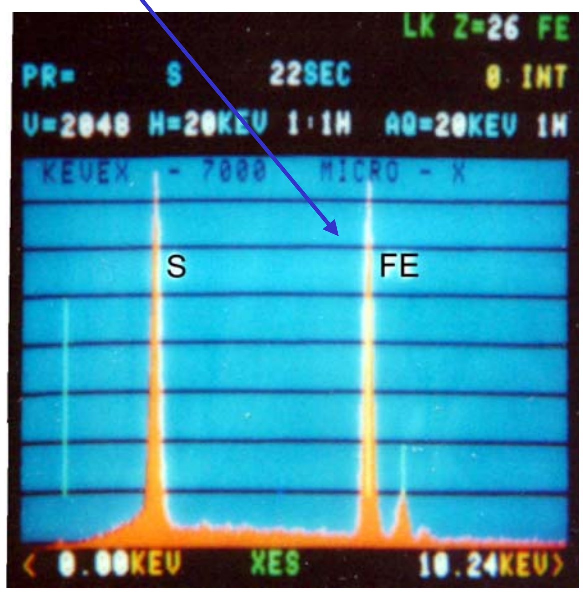
HCl →

dissolve FeS layer to expose underlying area

$$FeS + 2H^+ \longrightarrow Fe^{2+} + H_2S$$

Electrochemical reduction: $S^0 + 2e^- \xrightarrow{Fe^{2+}} FeS$

XES analysis of FeS layer



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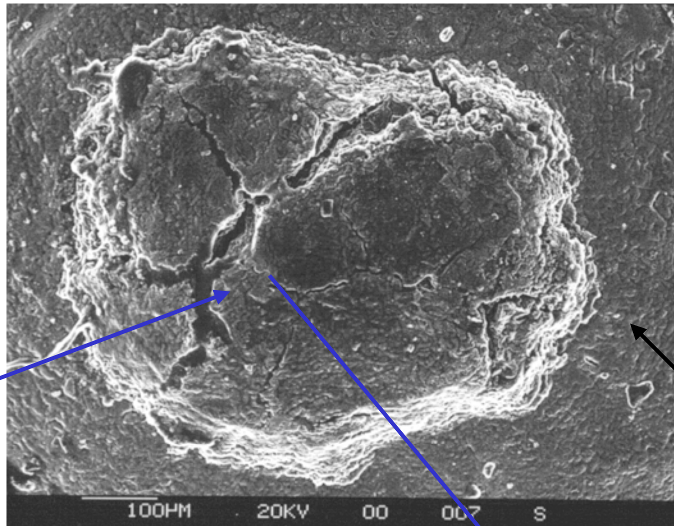
SEM ANALYSIS OF DIRECT ELECTROCHEMICAL REDUCTION OF SOLID SULFUR

FeS layer formed by reduction of sulfur

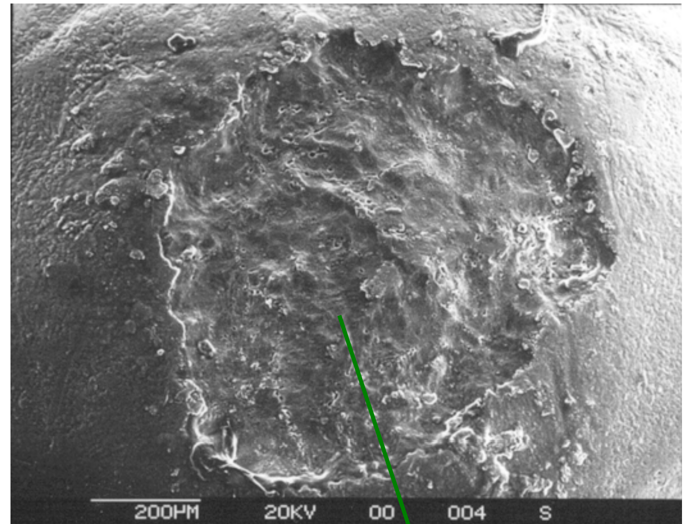


FeS

S^0

HCl

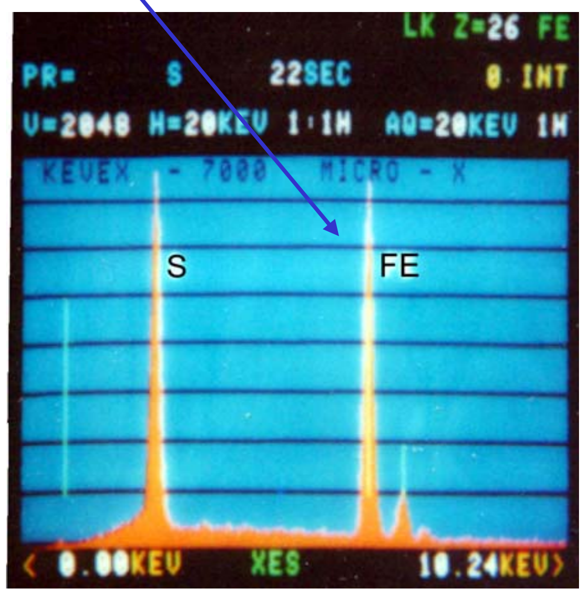
Dissolve FeS layer



Electrochemical reduction: $S^0 + 2e^- \xrightarrow{Fe^{2+}} FeS$

Remove FeS by acid: $FeS + 2H^+ \longrightarrow Fe^{2+} + H_2S$

XES analysis of FeS layer



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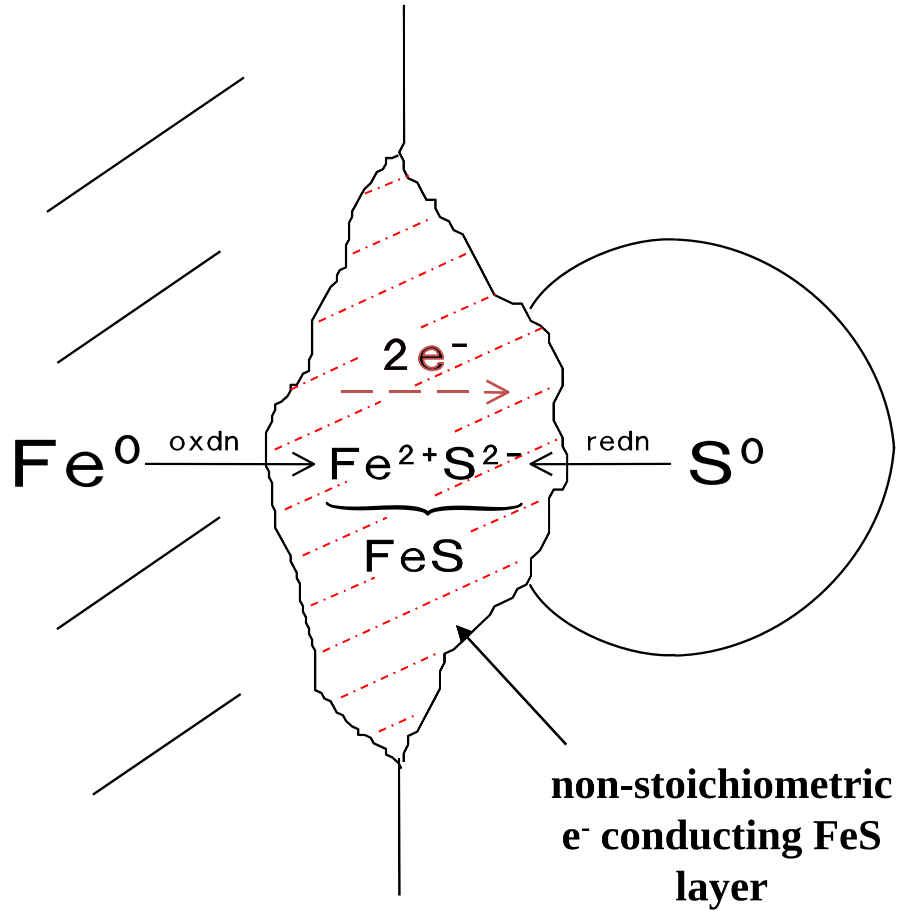
Conclusions:

a) Solid elemental sulfur consumed by electrochemical reduction

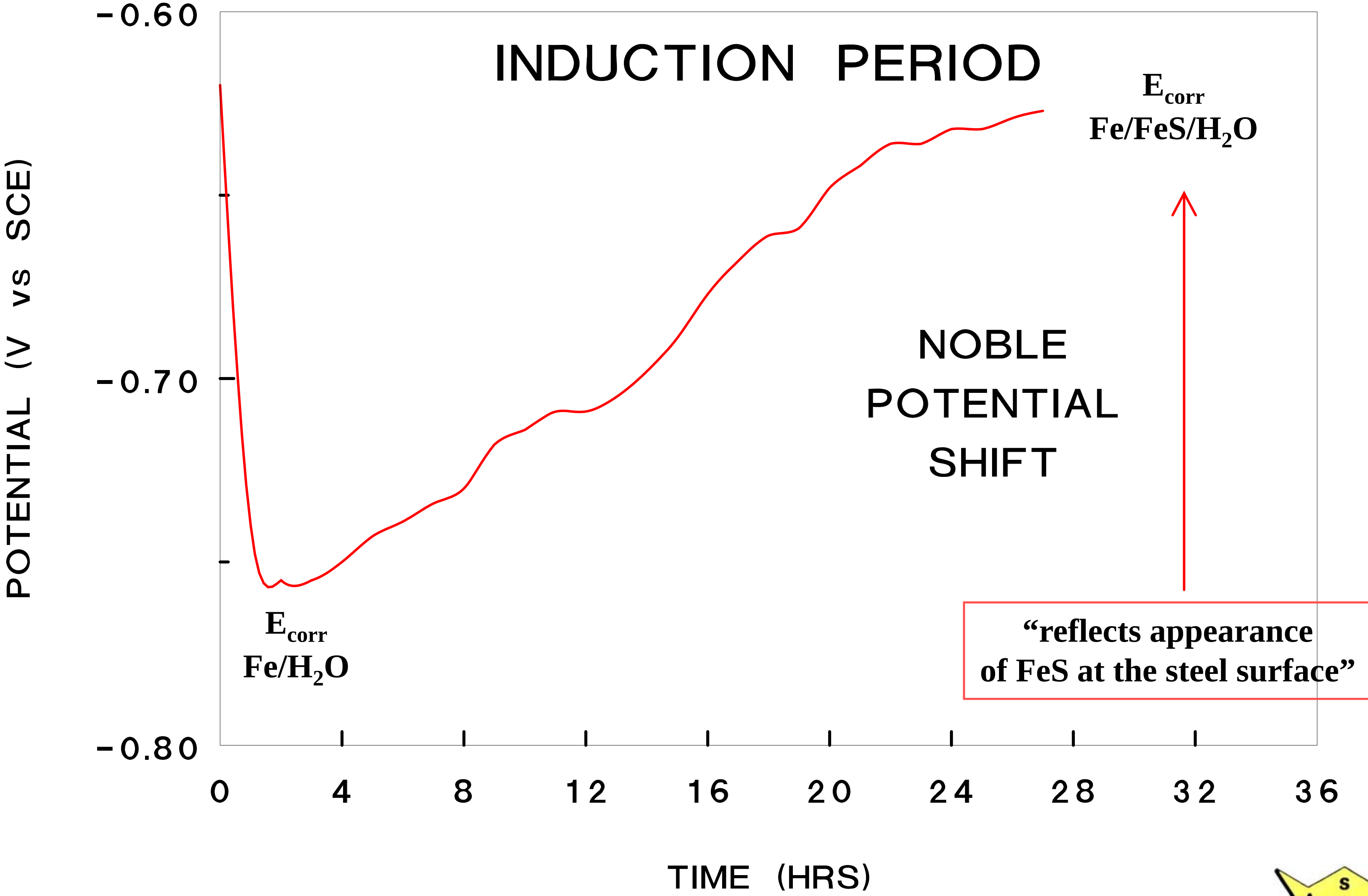
b) Evidence for e- conductivity of FeS layer

OVERVIEW OF STEEL/SULFUR (CONTACT) CORROSION



non-stoichiometric
e^- conducting FeS
layer

CORROSION POTENTIAL OF MILD STEEL VS TIME IN A SULFUR/H_2O ENVIRONMENT



MECHANISM OF THE INDUCTION PERIOD

a) Aqueous corrosion of carbon steel $\longrightarrow$ $\boxed{Fe^{2+}}$

b) Release of trapped H_2S from solid elemental sulfur

$$H_2S_x \longrightarrow H_2S_{(trap)} + S_{(x-1)}$$

$$H_2S_{(trap)} \longrightarrow \boxed{H_2S}$$

c) Disproportionation of $S_xO_y^{2-}$ species on oxidized surface of elemental sulfur

$$S_xO_y^{2-} + H_2O \longrightarrow \boxed{H_2S} + H_2SO_4$$

Appearance of FeS: $Fe^{2+} + HS^{-} \longrightarrow FeS + H^{+}$

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