Tests undertaken to explore applications of 125 ksi SMYS casing in sour environments

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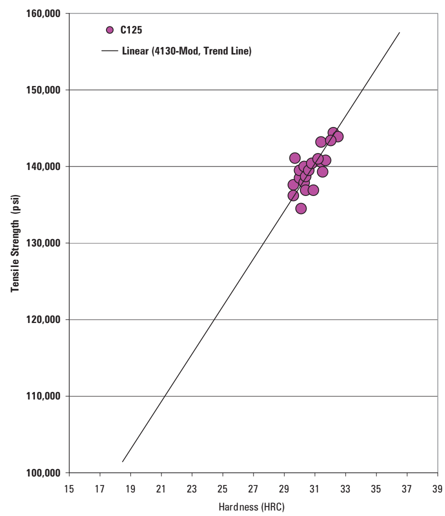
WITH THE CONTINUED exploration and development of deep, high-pressure, high-temperature reservoirs, the need for high-strength tubulars with sulfide stress cracking (SSC) resistance is ever increasing. The growing popularity of high-strength, SSC-resistant materials such as Grades T95, C100 and C110 is paving the way for a new generation of even higher-strength SSC-resistant casing products.

This article briefly summarizes the results of extensive testing undertaken to explore the possibilities of using 125 ksi specified minimum yield strength (SMYS) casing in sour or mildly sour environments.

- Yield strength window: 125,000 – 140,000 psi (862 – 965 MPa)
- Minimum tensile strength: 135,000 psi (931 MPa)
- Steel chemistry: modified AISI 4130
- Hardness maximum: 36 HRC
- Impact toughness: API minimum absorbed energy requirements for Grade Q125

The SSC resistance of the 125 ksi material was evaluated utilizing the NACE TM0177-96 Method-A and Method-D test protocols. Method-A and Method-D specimens were tested in solutions with H_2S concentrations of 3%, 7%, 10% and 100%.

This paper also details the key manufacturing steps necessary to produce a high-strength, SSC-resistant tubular product and the relationship between SSC resistance and various mechanical properties such as yield/tensile strength and hardness.



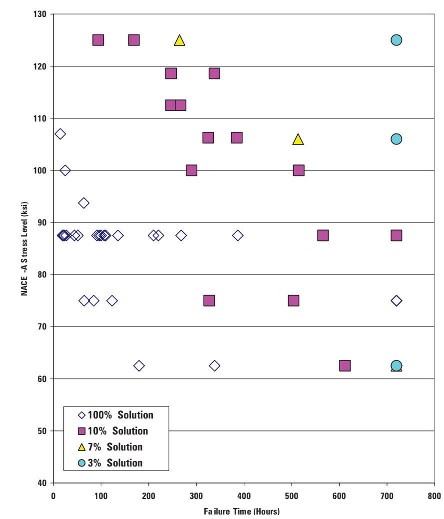


Figure 1 (left): Tensile strength as a function of hardness trend line for modified AISI 4130 steel chemistry. Figure 2: NACE Method A test results.

	C	Mn	P	S	Si	Cr	Mo
Min	0.26	0.35	-	-	0.18	0.90	0.75
Max	0.30	0.55	0.010	0.005	0.30	1.10	0.85

Table 1: Chemical composition of modified AISI 4130 steel.

	C	Mn	P	S	Si	Cr	Mo
Min	0.28	0.40	-	-	0.15	0.80	0.15
Max	0.33	0.60	0.035	0.040	0.30	1.10	0.25

Table 2: Chemical composition of standard AISI 4130 steel.

Heat Identification Letter	Heat Number	Outer Diameter (in)	Wall Thickness (in)	Mass (lb/ft)
A	262-007	13.625	0.625	86.86
B	262-009	13.625	0.625	86.86
C	262-010	13.625	0.625	86.86
D	262-011	13.625	0.625	86.86
E	262-012	13.625	0.625	86.86
F	162-007	7.625	0.500	38.08

Table 3: Heats of steel used in this study.

The need for higher yield strength casing with SSC resistance continues to increase as the petroleum industry develops deeper, higher pressure and higher temperature formations that may contain in situ H_2S or be susceptible to reservoir souring from water injection. The desired combination of strength and SSC resistance has in the past led to the development of grades such as T95, C100 and C110. These grades were seemingly impossible just 20 years ago, but with advancements in metallurgy and manufacturing technology, these high-strength, SSC-resistant grades are today routinely used by well designers with confidence in deep sour service applications. Grade C110 is currently the highest minimum yield strength material commercially available that is specifically intended for sour service.

EXPERIMENTAL PROCEDURE

Test material: The material utilized in this study is a modified American Iron and Steel Institute (AISI) 4130 carbon steel. This steel chemistry has a low-sulfur content and is produced using ultra-clean steel practices with vacuum degassing and alloy additions for inclusion shape control. The chemical composition of the modified AISI 4130 steel used in this study is shown in Table 1. The chemical composition for standard AISI 4130 steel is shown in Table 2. Testing was performed on 5 heats of 13.625 in. by 86.86 lb/ft (0.625 in.), and one heat of 7.625 in. by 38.08 lb/ft (0.500 in.) seamless casing that were heat-treated to Grade C125 attributes. Table 3 is a comprehensive listing of all heats used in this study.

Heat treatment: Heat-treating on the subject material was performed in a modern quench and temper operation. Austenitization was conducted in a gas-fired walking beam furnace at approximately 1,600ºF (871ºC). Quenching was accomplished using an inner-diameter/outer-diameter (ID/OD) water quenching system that provides the uniform martensitic microstructure necessary for maximum SSC resistance. Tempering was conducted in a second gas-fired walking beam furnace using the highest tempering temperatures allowable while still maintaining uniform hardness and Grade C125 mechanical properties. The Grade C125 material was quenched and tempered twice, which previous research has shown to enhance SSC resistance. All material was hot straightened at no less than 750°F.

Mechanical properties: Yield/tensile strength, Charpy V-notch toughness and hardness attributes were evaluated in accordance with the standard test procedures listed in ISO 11960 /API Spec 5CT. Figure 1 shows the historic tensile strength vs. hardness trend line for the modified AISI 4130 steel chemistry. This trend line was developed using existing tensile and hardness data from other quenched and tempered material such as Grades T95, C100 and C110. The tensile vs. hardness data are also shown in Figure 1. The trend line should not be interpreted as definitive. Figure 1 indicates that the high hardness values obtained in the subject heats are to be expected at tensile strengths exceeding 130 ksi. The yield strength, tensile strength and hardness data are shown in Table 4.

Heat	Yield Strength (psi)	Tensile Strength (psi)	Y/T Ratio	Hardness (HRC)	Lot
A	132,500	140,000	0.946	30.3	34340
A	126,300	137,900	0.916	30.3	34340
B	134,950	139,300	0.969	31.5	34341
B	133,300	138,500	0.962	30.0	34342
B	130,200	137,200	0.949	30.5	34342
B	129,950	138,200	0.940	30.2	34348
B	134,080	141,100	0.950	29.7	34348
C	135,300	140,600	0.962	31.4	34339
C	129,100	138,200	0.934	30.7	34339
C	132,240	141,200	0.937	30.9	34349
C	133,340	138,300	0.964	None	34339
C	127,820	137,700	0.928	30.5	34339
C	126,600	137,000	0.924	30.8	34339
C	132,000	138,700	0.952	30.4	34349
C	133,540	138,500	0.964	None	34349
C	132,830	139,200	0.954	30.9	34349
C	136,440	143,200	0.953	31.4	34349
D	133,700	140,800	0.950	31.7	34345
D	137,450	140,400	0.979	30.8	34346
D	130,810	138,900	0.942	29.4	34346
D	133,200	139,500	0.955	30.0	34350
E	132,990	139,500	0.953	30.6	34343
E	129,340	136,900	0.945	30.9	34343
E	135,370	139,400	0.971	31.5	34344
E	134,110	138,100	0.971	29.8	34347
E	133,650	136,900	0.976	30.4	34347
F	128,160	141,000	0.909	31.12	O-182
F	134,170	143,900	0.932	32.5	F-189

Table 4: Yield, tensile and hardness data for all heats.

SSC properties: Two different test methods were employed to evaluate SSC resistance: the NACE Method-A standard tensile test and the NACE Method-D standard Double Cantilever Beam (DCB) test. All testing was performed in accordance with NACE TM0177-96 by a single laboratory. Both NACE Method-A and NACE Method-D specimens were tested in standard Solution-A and in a modified Solution-A. The modified Solution-A had H_2S concentrations of 3%, 7% and 10%. NACE Method-A specimens were subjected to stresses ranging from 50% to 100% of SMYS by means of a calibrated loading ring.

Fracture toughness: The fracture toughness of this material was thoroughly investigated using Charpy V-notch impact testing. The material's impact toughness was evaluated for both the transverse and longitudinal directions using full size (10 mm by 10 mm) Charpy

V-notch specimens. Transverse Charpy V-notch testing (Table 5) was performed at 14°F (-10°C).

Standard NACE Solution-A, NACE Method-A Test Results (100% H_2S): All Method-A testing was performed in accordance with NACE TM0177-96. Specimens were orientated longitudinally and stressed at a percentage of the Grade C125 SMYS. The testing was performed on Heats A, B, C, D and E in the standard saturated Solution-A (100% H_2S) and in modified concentrations of Solution-A (3%, 7% and 10% H_2S). Heat F was tested only in the standard Solution-A (100% H_2S). Timers were not used for any of the 10% and 100% H_2S test cells; only approximate failure times are given for some of the samples shown in Tables 6 through 11. The hardness values given for each of the test specimens in Tables 6 through 13 were determined by making 4 HRA impressions, spaced at 90° intervals on the specimen surface. Readings were averaged, corrected for curvature and converted to HRC. Hardness testing was performed prior to H_2S exposure.

Three specimens from each heat were stressed at 87.5 ksi (70% SMYS) and tested in the 100% H_2S solution. All 15 specimens failed; results are shown in Table 6. Sample survival time ranged from approximately 21 hours to 398 hours. One sample from several heats were stressed at 75.0 ksi (60% SMYS) and tested in the 100% H_2S solution. Results are shown in Table 7. One sample from Heat A, B, C, D and E was stressed at 62.5 ksi (50% SMYS) and tested in the 100% H_2S solution. Of the 5 specimens, 3 successfully passed with no signs of cracking. Results are shown in Table 8. Specimens from Heat F were subjected to stress levels ranging from 93.75 to 107 ksi (75% to 85.6% SMYS) while in the 100% H_2S solution. All specimens failed; results are shown in Table 9.

Modified NACE Solution-A, NACE Method-A Test Results (3%, 7% and 10% H_2S): Tables 10, 11, 12 and 13 detail the results of testing Method-A specimens in the less acidic pH and reduced H_2S concentration Solution-A (3%, 7% and 10% H_2S concentrations).Heat E was tested at 5 different stress levels ranging from 100 to 125 ksi (80% to 100% SMYS) while in the 10% H_2S solution (2 specimens at each stress level). All 10 specimens failed; results are shown in Table 10. Since no specimens from Heat E stressed at 100 to 125 ksi (80% to 100% SMYS) in the milder solution

Heat	Sample 1 (ft-lbs)	Sample 2 (ft-lbs)	Sample 3 (ft-lbs)	Average (ft-lbs)
A	80	81	77	79
B	78	76	81	78
B	88	86	92	89
C	82	75	75	77
C	74	74	77	75
C	77	80	80	79
D	88	92	92	90
D	85	82	87	84
E	87	89	86	87

Table 5: Charpy V-notch impact results, transverse, full-size specimens, 14ºF (-10ºC).

Heat	Sample ID	Hardness (HRC)	Failure Time (Hr)	Solution pH	
				Start	Finish
A	Y-191	30.7	104 ± 8	2.7	3.0
A	A-192	30.6	21	2.7	3.0
A	Z-191	30.4	106.5	2.7	3.0
B	B-192	31.3	109.5	2.7	3.0
B	C-192	31.0	220.3	2.7	3.0
B	D-192	31.2	135.5	2.7	3.0
C	T-191	30.9	91.3	2.7	3.0
C	P-192	30.6	25.4 ± 2.5	2.7	3.0
C	R-192	32.7	51.1	2.7	3.0
D	H-192	32.3	45 ± 4	2.7	3.0
D	I-192	31.4	107 ± 7	2.7	3.0
D	S-192	31.5	23 ± 4	2.7	3.0
E	E-192	31.4	210.0	2.7	3.0
E	F-192	30.6	34 ± 7	2.7	3.0
E	M-192	30.6	398 ± 11	2.7	3.0

Table 6: Results for NACE Method-A, Standard Solution-A (100% H_2S) at 87.5 ksi (70% SMYS).

Heat	Sample ID	Hardness (HRC)	Failure Time (Hr)	Solution pH	
				Start	Finish
A	A-192B	31.0	**No Failure**	2.7	3.7
B	C-192B	32.0	**No Failure**	2.7	3.6
C	P-192B	31.5	64.5	2.7	3.4
D	I-192B	32.0	123.0	2.7	3.6
E	F-192B	31.2	84.5	2.7	3.6

Table 7: Results for NACE Method-A, Standard Solution-A (100% H_2S) at 75 ksi (60% SMYS).

(10% H_2S) passed the test, Heats A, B, C, D and E were tested with the same 10% H_2S concentration but with lower stress levels: 62.5 ksi (50% SMYS), 75.0 ksi (60% SMYS) and 87.5 ksi (70% SMYS). All specimens failed. Results are shown in Table 11. Sample Z-191B, from Heat A, did not fracture into 2 distinct halves typical with Method-A failures. Multiple cracks were found along the sample gage length and fillet region, rendering the test invalid. Sample S-192 fractured in the fillet region also rendering this test invalid. Specimens from Heat C were tested in 3% and 7% H_2S concentrations at 3 different stress levels: 62.5 ksi (50% SMYS), 106 ksi (85% SMYS), and 125 ksi (100% SMYS). None of the specimens tested in the 3% H_2S solution failed; results are shown in Table 12. The 2 specimens subjected to the 85% and 100% stress levels in the 7% H_2S solution failed. Results are shown in Table 13. The failure times listed in Tables 12 and 13 are exact because timers were used on these test cells.

Standard NACE Solution-A, NACE Method-D Test Results (100% H_2S): Method-D specimens from Heats A, B, C, D and E were tested in standard Solution-A (100% H_2S). Results are shown in Table 14. Heat B had no valid specimens; all were disqualified for excessive edge cracking or non-planar cracking. Over 50% of the specimens for the other 4 heats were disqualified. Specimens from Heat F suffered the same disqualification rate. Roughly half of the specimens were disqualified due to excessive edge cracking or non-planar cracking. Results are shown in Table 15.

Modified NACE Solution-A, NACE Method-D Test Results (10% H_2S): Method-D testing was performed on Heats A, B, C, D and E in standard Solution-A (100% H_2S) and modified Solution-A (10% H_2S). Heat F was tested only in standard Solution-A (100% H_2S). For each heat, 4 specimens were machined from a single 5 in.-by-6 in. panel of material. The hardness values shown in Tables 14, 15 and 16 are the average of 6 HRC measurements taken directly on the DCB specimen using a precision hardness tester. Hardness measurements were made prior to H_2S exposure. Results are shown in Table 16. Over half the specimens were disqualified for excessive edge cracking. With the modified Solution-A (10% H_2S), crack pinning and non-planar crack propagation were not observed.

Heat	Sample ID	Hardness (HRC)	Failure Time (Hr)	Solution pH Start	Solution pH Finish
A	Y-191B	31.1	**No Failure**	2.7	3.6
B	B-192B	31.8	338.3	2.7	3.7
C	T-191B	31.3	**No Failure**	2.7	3.7
D	H-192B	32.6	179.7	2.7	3.8
E	E-192B	32.0	**No Failure**	2.7	3.7

Table 8: Results for NACE Method-A, Standard Solution-A (100% H_2S) at 62.5 ksi (50% SMYS).

Heat	Sample ID	Hardness (HRC)	Applied Stress (ksi)	% SMYS	Failure Time (Hr)	Solution pH Start	Solution pH Finish
F	0-182A	32.2	100	80	24.57	2.7	3.4
F	0-182B	32.4	107	86	14.23	2.7	3.4
F	0-182C	32.5	87.5	70	275 ± 7	2.7	3.8
F	0-182D	32.4	93.75	75	63.62	2.7	3.7

Table 9: Results for NACE Method-A, Standard Solution-A (100% H_2S).

Heat	Sample ID	Hardness (HRC)	Applied Stress (ksi)	% SMYS	Failure Time (Hr)	Solution pH Start	Solution pH Finish
E	A-193A	31.7	100	80	290	3.5	3.9
E	B-193A	31.7	100	80	515	3.5	4.2
E	C-193A	32.1	106.25	85	325	3.5	4.0
E	D-193A	31.8	106.25	85	385	3.5	4.1
E	E-193A	31.4	112.5	90	247	3.5	3.9
E	F-193A	31.6	112.5	90	267	3.5	4.0
E	G-193A	31.8	118.75	95	341 ± 3	3.5	4.1
E	H-193A	31.6	118.75	95	252 ± 5	3.5	3.9
E	I-193A	31.7	125.0	100	112 ± 18	3.5	3.7
E	J-193A	31.8	125.0	100	179 ± 10	3.5	3.9

Table 10: Results for NACE Method-A, Modified Solution-A (10% H_2S).

Heat	Sample ID	Hardness (HRC)	Applied Stress (ksi)	% SMYS	Failure Time (Hr)	Solution pH Start	Solution pH Finish
A	Z-191B	30.6	87.5	70	720 (Invalid)	3.5	4.3
B	D-192B	31.3	62.5	50	612	3.5	4.1
C	R-192B	32.9	87.5	70	566	3.5	4.2
D	S-192B	31.8	75	60	327 (Invalid)	3.5	4.2
E	M-192B	30.5	75	60	504	3.5	4.1

Table 11: Results for NACE Method-A, Modified Solution-A (10% H_2S).

Heat	Sample ID	Hardness (HRC)	Applied Stress (ksi)	% SMYS	Failure Time (Hr)	Solution pH Start	Solution pH Finish
C	0-259-1	31.3	125.0	100	**No Failure**	3.5	4.50
C	0-259-2	31.5	106.0	85	**No Failure**	3.5	4.49
C	0-259-3	31.6	62.5	50	**No Failure**	3.5	4.48

Table 12: Results for NACE Method-A, Modified Solution-A (3% H_2S).

CONCLUSIONS

• For the NACE Method-A specimens that failed, the survival time was significantly increased when the H_2S concentration was decreased from 100% to 10% H_2S. A comparison of the same material

Heat	Sample ID	Hardness (HRC)	Applied Stress (ksi)	% SMYS	Failure Time (Hr)	Solution pH	
						Start	Finish
C	0-259-4	31.5	125.0	100	264.6	3.5	4.16
C	0-259-5	31.5	106.0	85	513.44	3.5	4.28
C	0-259-6	31.6	62.5	50	**No Failure**	3.5	4.27

Table 13: Results for NACE Method-A, Modified Solution-A (7% H_2S).

Heat	Sample ID	Hardness (HRC)	K_{ISSC} ($Ksi\sqrt{in}$)					Solution pH	
			1	2	3	4	Average	Start	Finish
A	Y-191	31.10	14.9	14.0	(a)	(a)	14.45	2.7	3.7
B	B-192	31.45	(a)	(a)	(a)	(a,b)	None	2.7	3.7
C	T-191	30.9	15.8	(a,b)	(a)	(a,b)	15.8	2.7	3.7
D	H-192	32.00	(a)	(a,c)	15.8	(a)	15.8	2.7	3.7
E	E-192	31.30	16.7	(a,b)	(a,c)	14.5	15.60	2.7	3.7

Table 14: Results for NACE Method-D, Standard Solution-A (100% H_2S).

Heat	Sample ID	Hardness (HRC)	K_{ISSC} ($Ksi\sqrt{in}$)					Solution pH	
			1	2	3	4	Average	Start	Finish
F	0-182	32.03	(a)	(b)	15.9	(b)	15.9	2.7	3.8
F	F-189	33.57	11.9	(a)	10.8	9.9	10.83	2.7	3.8

Table 15: Results for NACE Method-D, Standard Solution-A (100% H_2S).

Heat	Sample ID	Hardness (HRC)	K_{ISSC} ($Ksi\sqrt{in}$)					Solution pH	
			1	2	3	4	Average	Start	Finish
A	Y-191	31.1	(a)	(a)	(a)	22.1	22.1	3.5	4.1
B	B-192	31.40	(a)	22.4	21.4	(a)	21.90	3.5	4.1
C	T-191	30.85	20.6	(a)	(a)	22.9	21.75	3.5	4.1
D	H-192	32.40	(a)	(a)	(a)	22.5	22.5	3.5	4.1
E	E-192	31.35	22.4	(a)	(a)	22.4	22.40	3.5	4.1

Table 16: Results for NACE Method-D, Modified Solution-A (10% H_2S).

Heat	Applied Stress, ksi (% SMYS)	Failure Time (Hr) Standard Solution (100% H_2S)	Failure Time (Hr) Modified Solution (10% H_2S)
A	87.5 (70)	106.5	720 (Failing)
C	87.5 (70)	51	566
D	75.0 (60)	123	327
E	75.0 (60)	84	504
B	62.5 (50)	338.3	612

Table 17: Comparison of specimen survival time in different solutions.

tested at the same stress level in 2 different solutions is shown in Table 17.

• The NACE Method-A sample survival time as a function of the applied stress level for the various H_2S concentrations used in this study. Only approximate times were available for many of the tests; therefore, Figure 6 was developed using the most conservative value given for a particular specimen failure time frame. The relationship between sample survival time and stress level for specimens tested in the 10% H_2S and 7% H_2S solutions is consistent with work done by other investigators.

• At reduced stress levels, the material does not consistently pass the NACE Method-A test in the standard NACE Solution-A (100% H_2S).

• The 3 NACE Method-A specimens tested in the modified NACE Solution-A (3% H_2S) successfully passed (Table 12). This is quite encouraging considering the specimens were stressed at levels as high as 106 ksi (85% SMYS) and 125 ksi (100% SMYS).

• The NACE Method-D testing showed a marked improvement in performance when the H_2S concentration was lowered from 100% to 10%. For all heats, the average increase in K_{ISSC} was 6.8 $Ksi\sqrt{n}$.

• The K_{ISSC} values obtained from testing in the 100% H_2S solution are consistent with the HRC/K_{ISSC} relationship seen in previous work involving Grades T95, C100 and C110 manufactured using the same steel chemistry and manufacturing techniques.

• The high disqualification rate of DCB specimens, in both solutions (standard and modified NACE Solution-A), is attributed to the materials' high tensile strength.

• Both the NACE Method-A and NACE Method-D testing exhibited in this research provides strong evidence that a high-strength casing with 125 ksi minimum yield strength (C125), produced using high-quality steel and advanced manufacturing techniques, could be used in mildly sour environments. Well designers are strongly urged to evaluate the fit-for-purpose attributes of this experimental product to each specific set of well conditions.

• The microstructure exhibited in Figures 3, 4 and 5 is typical of quenched and tempered martensite, consistent with other high-strength tubular products such as Grade C110.

• Fracture toughness is always a concern when utilizing high-strength tubulars, even in non-H_2S bearing wells. The ductile-to-brittle transition curves shown in Figure 2 illustrate that this material has a high resistance to crack propagation in both the transverse and longitudinal directions. The material impact toughness far exceeds the minimum of 22 ft-lbs (30 J) (transverse direction) and 45 ft-lbs (60 J) (longitudinal direction) per ISO11960/API 5CT 7.5.49 for a 13.625 in. by 86.86 lb/ft (0.625 in.) Grade Q125 at 32°F (0°C).

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