LOW MANGANESE SOUR SERVICE LINEPIPE STEEL

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Keywords: Sour Service, Linepipe, Niobium, Manganese, Mechanical Properties, Segregation, Inclusions, HIC, Ca Treatment, ERW Pipe, Charpy Toughness, Stress Relaxation

Abstract

Linepipe steel technology and metallurgy have evolved over the past four decades since the spectacular failure of a BP line in the Umshaif (Arabian) Gulf. The X65 steel in question was severely controlled rolled and despite having a sulfur content of 0.005 percent, considered very low at that time, featured large quantities of MnS stringer inclusions. Remedial measures involved lowering manganese to below 1.20 percent, development of inclusion shape control technologies and avoidance of low temperature finishing practices. With time, the familiar "BP Solution" (now Solution B in NACE TM0284), was replaced by the more aggressive NACE solution and a new round of steel development occurred. Carbon contents were reduced, sulfur was lowered to below 0.0020 percent, steel cleanliness improved and alloying with chromium and copper became widespread. Additionally, control of pearlite banding and phosphorus segregation was coupled with improved continuous casting practices and the steels became highly resistant to HIC. In a relatively recent development, steels with ultra-low manganese contents (<0.30%) have been developed, which are more forgiving of residual sulfur content and variable casting machine performance and other manufacturing variables. The present paper summarizes the metallurgical basis of the ultra-low manganese concept and presents recent results.

Introduction

Worldwide reports of serious failures due to sulfide stress cracking and hydrogen induced stepwise cracking in pipelines and other components date back to 1954 according to tabulations taken from the literature, Table I. Problems in pipelines in the United States have been less serious and costly than elsewhere, according to a review of US-DOT statistics made by the author in the late 1980s, Table II [1]. However, notable failures have occurred in Canada, Saudi Arabia, Qatar and the Arabian Gulf in the past forty years. Details known to the author are presented in Table III [1].

Table I. Examples of Failure by Hydrogen Induced Cracking

No.	Location	Plant	Materials (Steel)	Used conditions and environment	Operating	
					Beginning Date	Failure Discovered
1	U.S.A.	Sour Refinery (Crude oil) Pressure vessel (sour gasoline)	Mild steel (Y.P. 28 kg/mm^2) (T.S. 42 kg/mm^2) C 0.24, Si 0.06, Mo 0.58 P 0.009, S 0.028, Al 0.008	Phillips Petroleum Co. Ltd. Examples of blistered vessel: over 50 °C, $H_2S + H_2O$, low operation pressure	Unknown	Unknown
2	Japan	Heavy oil desulfurization apparatus, condenser shell	Mild steel (SB42) C 0.18, Si 0.30, Mn 0.80, P <0.030, S <0.030	$H_2S + H_2O$, 38 °C Operation pressure 48 kg/cm^2	5/1971	6/1973
3	Japan	Desulfurization apparatus	Mild steel (SB42) Low alloy steel (Cr 1.25, Mo 0.5)	$H_2S + H_2O$ <50 °C Operation pressure 32 kg/cm^2	4/1966	8/1968
4	Japan	Desulfurization apparatus	Mild steel (SB42) C 0.17, Si 0.26, Mn 0.78, P 0.015, S 0.018, Cu 0.09	$H_2S + H_2O$ (condensate) Operation pressure 17-33 kg/cm^2	4/1964	9/1965
5	Japan	Desulfurization apparatus	Mild steel (SB42)	25-110 °C Operational pressure 33 kg/cm^2	11/1961	8/1967
6	U.S.A.	Refinery vessel	Carbon steel	Shell Oil H_2S, CO_2, NH_3, H_2O	Unknown	1954
7	U.S.A.	Linepipe (Barkerdom gathering)	API 5LX52 (24” x 0.271” wt , SAW) 1.75 – 1.95 mm cold worked	El Paso Natural Gas Co. Ltd. Natural Gas, CO_2 15%, H_2S 1%	1954	1954
8	FRG	Linepipe	API 5LX42 (ERW) Annealed and Straightened	H_2S max. 0.95%, CH_2 80-85% CO_2 8.7% Operation pressure 45.5 kg/cm^2	1/1961	1/1961
9	Italy	Refinery	Mild steel C 0.12, Si 0.26, Mn 0.47, P 0.017, S 0.018	H_2S 10%, H_2O 5%, gasoline	Unknown	Unknown
10	Arabia	Linepipe on land (sour gas)	API 5LSX42 As rolled spiral	H_2S 3.4 vol% CO_2 8.8 vol% CH_4	1974	1974

Table II. DOT Sour Service Failures 1970-1986

Company	Year Installed	Dia (in)	Wall Thickness (in)	Yield Strength (ksi)	Grade	Failure Pressure (psig)	Design Pressure (psig)	State	Damage ($)
Panhandle Eastern	1930	22 DSAW	0.344	30	Unknown	397	500	Hutchinson Co., TX	27,500
Phillips	Unknown	10 ERW	0.105	35	Unknown	25	390	Midland, TX	5,000
Collet Systems	1985	3 SMLS	0.300	35	API 5L Grade B	1000	2552	Washington Co., AL	Unknown
Phillips (formally El Paso)	1971	18 ERW	0.188	35	API 5L	90	175	Ector Co., TX	11,500
Columbia	1960	16 ERW	0.281	52	API 5L X52	745	825	Schuyler, N.Y.	30,000
Trunkline	1959	10.75 ERW	0.365	35	API 5L Grade B	280	970	Galveson, TX	10,200

Table III. Summary of Sour Gas Failures

Year of Failure	Reference	Owner	Type	Steel Grade	Dia (in)	Failure Mechanism	Cause	Other
1972	Umshaif (Arabian Gulf)	British Petroleum	DSAW 0.500" Wall	X65	30	HIC	Elongated MnS inclusions. Severe rolling of low S steel (S 0.004-0.010%)	First failure in "modern" linepipe. Start of routine HIC testing (B.P. Solution)
1978	Stolberg Line (Alberta)	Aquitane	DSAW		?	HIC and SSC 350,000 ppm H_2S	Semi-killed steel with silicate stringer and high sulfur (0.025–0.030%)	Aqutaine specs rewritten around fully-killed steel and 0.004%S max.
1978/80	Saudi Gas Lines	ARAMCO	DSAW	X52	Various	HIC 20000-50000 ppm H_2S	Elongated MnS inclusions	HIC testing introduced for screening all suppliers
1979	Waterton (Alberta)	Shell, Canada	DSAW		?	HIC and SSC	Semi-killed steel with silicate stringer. Excessive impurities S 0.030, P 0.025 and silicates	HIC testing introduced, S max. 0.004%, HV 238 500g
July 1981	Grizzly Lateral (British Colombia)	W.Coast Transmission	DSAW (spiral) 0.375" wall	X52	20	Weld metal and HAZ 275,000 ppm H_2S 136,500 ppm CO_2	SSC, HV 420 (43 HRC) HIC, High Sulfur with stringers, Semi-killed steel	CSA Standard Z245.2 rewritten to include sour service testing. West Coast Spec. Revised to limit sulfur to 0.004% and HV 238
1981	Cherry Creek (Williston, ND)	Aminoil	ERW		10	SSC 54000 ppm H_2S	Unannealed seam, High Hardness	Manufacturing defect did not meet API 5L Specification
1981	Das Island, Qatar	Qatar Petroleum	DSAW 0.625" wall	X60	24	Stress assisted HIC/SSC	High HAZ hardness	

Perhaps the most significant failure occurred in 1972 in a BP line installed in the Umshaif Gulf (Arabian Sea). The steel involved had low sulfur and carbon contents and was considered state-of-the-art at the time. Severe stepwise cracking led to failure after less than one month in service.

Research into the cracking mechanism gave birth to the BP or "Cotton" test (promulgated by the late Harry Cotton). The test was eventually standardized by NACE in 1984 (TM-02-84) [2]. The methodology was first updated in 1987 [TM-02-84 (87)] and further changes have occurred since. As part of the evolution of this test method, the pH of the test solution was reduced from 5.2 to 2.8 (NACE TM-01-77(90) [3] solution) to facilitate proper screening of advanced highly resistant modern steels. Additionally, allowance for sample flattening has been deleted [4].

Steel Development

During the past 40 years steelmaking and rolling technology advanced rapidly due to the demand for linepipe suitable for use in very severe environments. The applicability of measures to counteract corrosive CO_2 and H_2S environments is shown in Figure 1 as a function of H_2S concentration and service pressure. A more complete hierarchy of mitigation measures is presented in Figure 2 [1].

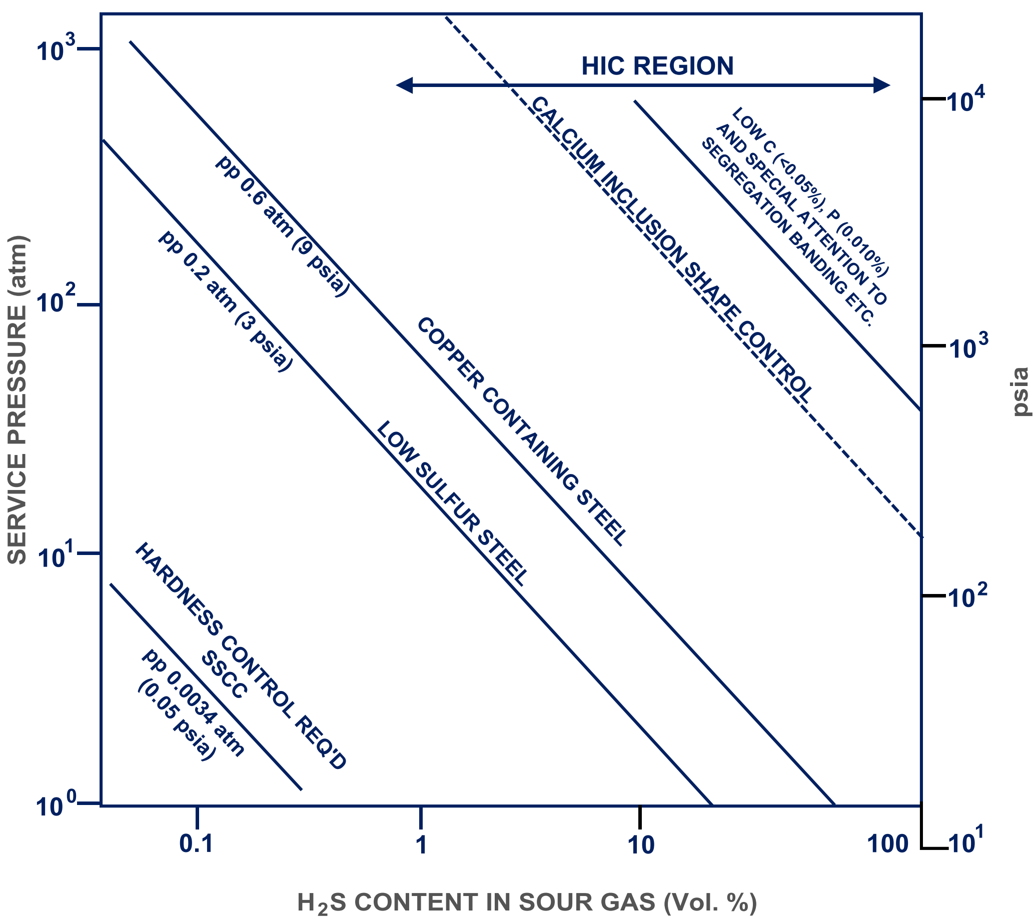


Figure 1. Metallurgical approaches for mitigating hydrogen sulfide as a function of H_2S content and sevice pressure.

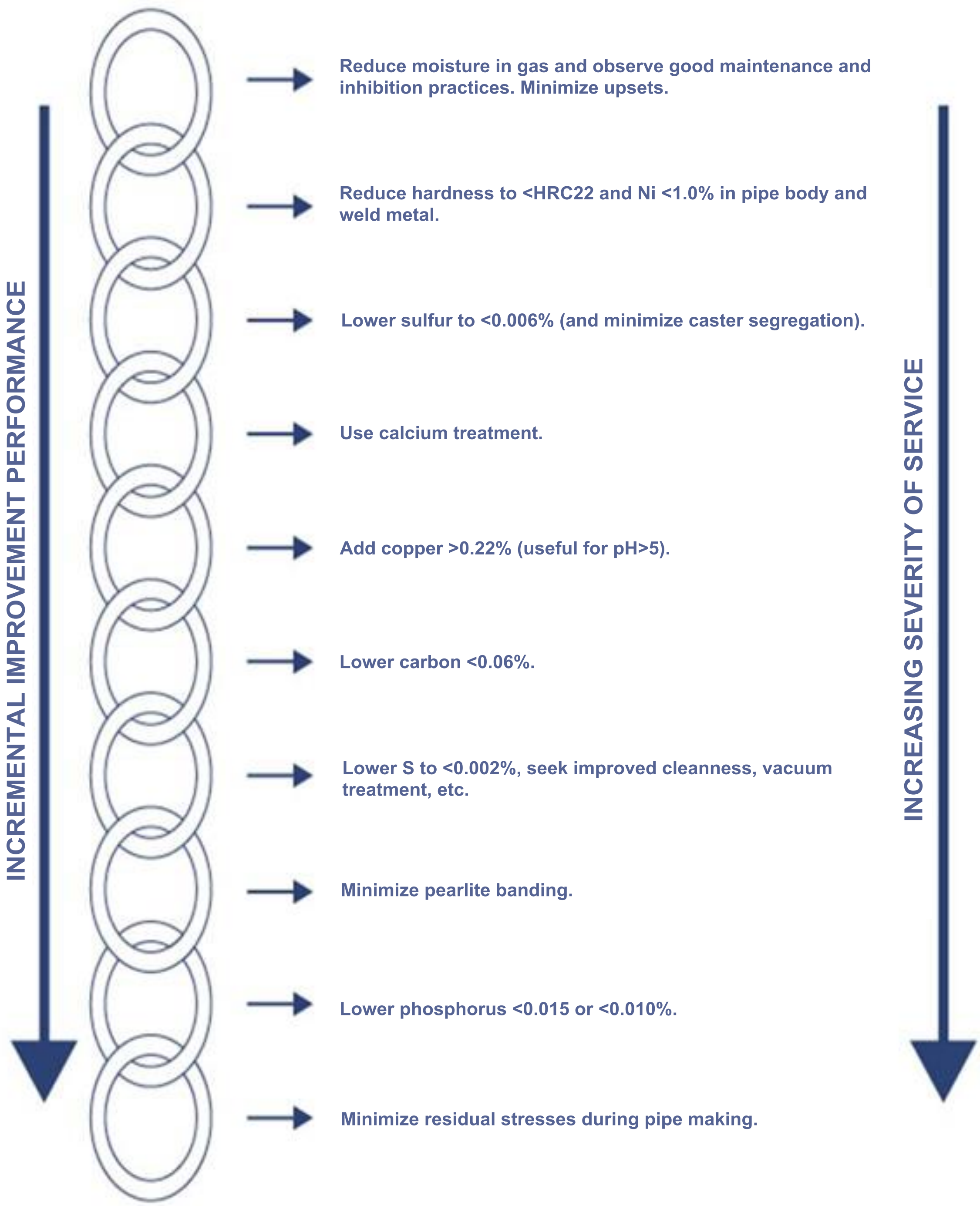


Figure 2. Hierarchy of mitigation measures for sour service linepipe [1].

Reduction of hardness is the first line of defense for preventing sulfide stress cracking (SSC). At higher H_2S concentrations, the hydrogen induced stepwise cracking (HIC) regime is dominant and the industry practice is to use reduced sulfur levels (<0.005%) for moderately sour applications (pH 5.2 or Solution B test conditions) and less than 0.0020% sulfur when Solution A is specified. Additionally, inclusion shape control elements such as calcium, rare earths and zirconium are utilized to prevent the formation of elongated manganese sulfide inclusions. Simultaneously, manganese contents are typically reduced to less than 1.20 percent, Figure 3 [5], to minimize centerline segregation, especially when older continuous casting machines are being utilized.

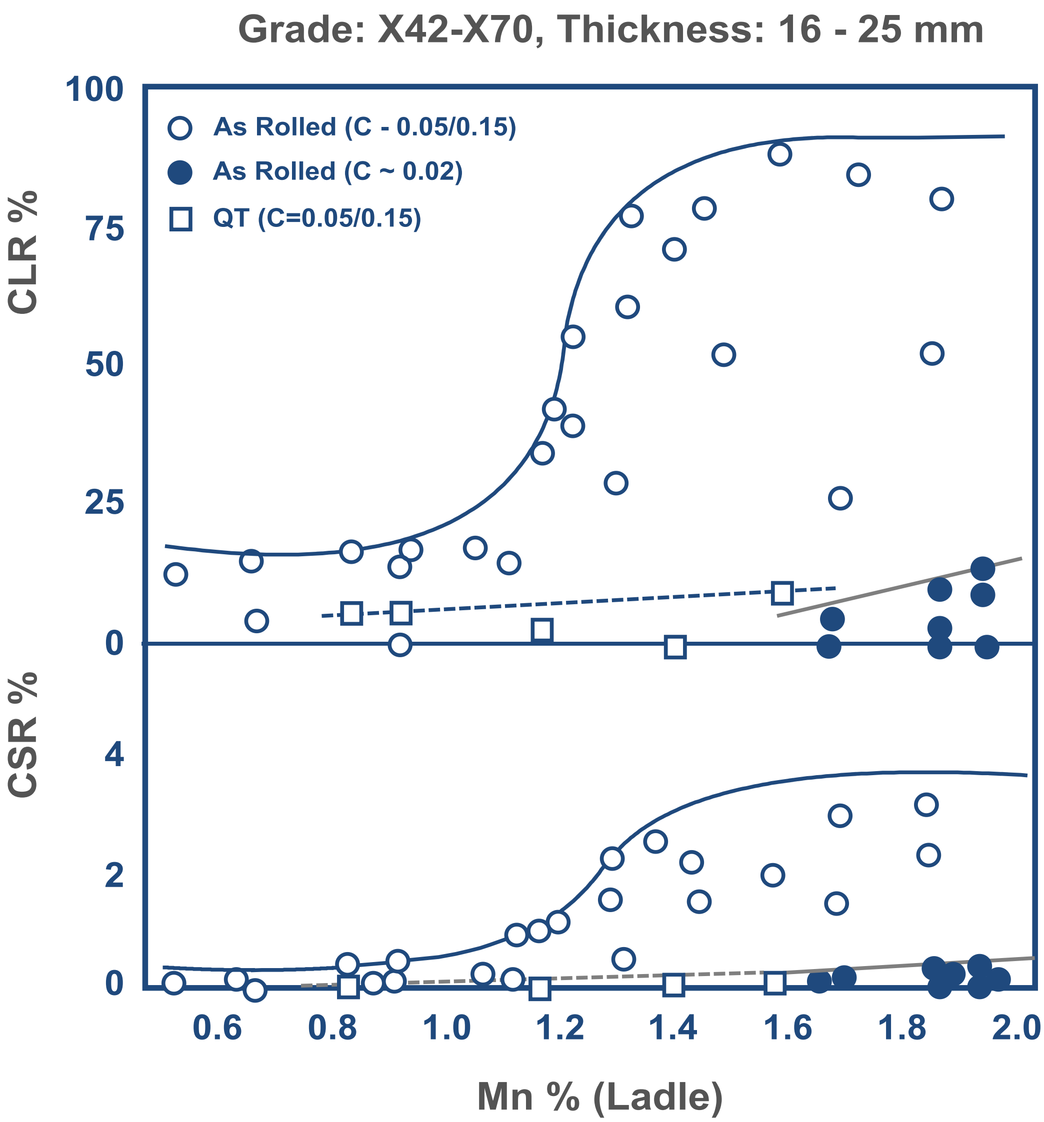


Figure 3. Effect of Mn on HIC susceptibility [5].

The benefit of calcium treatment in reducing HIC is illustrated in Figures 4 and 5.

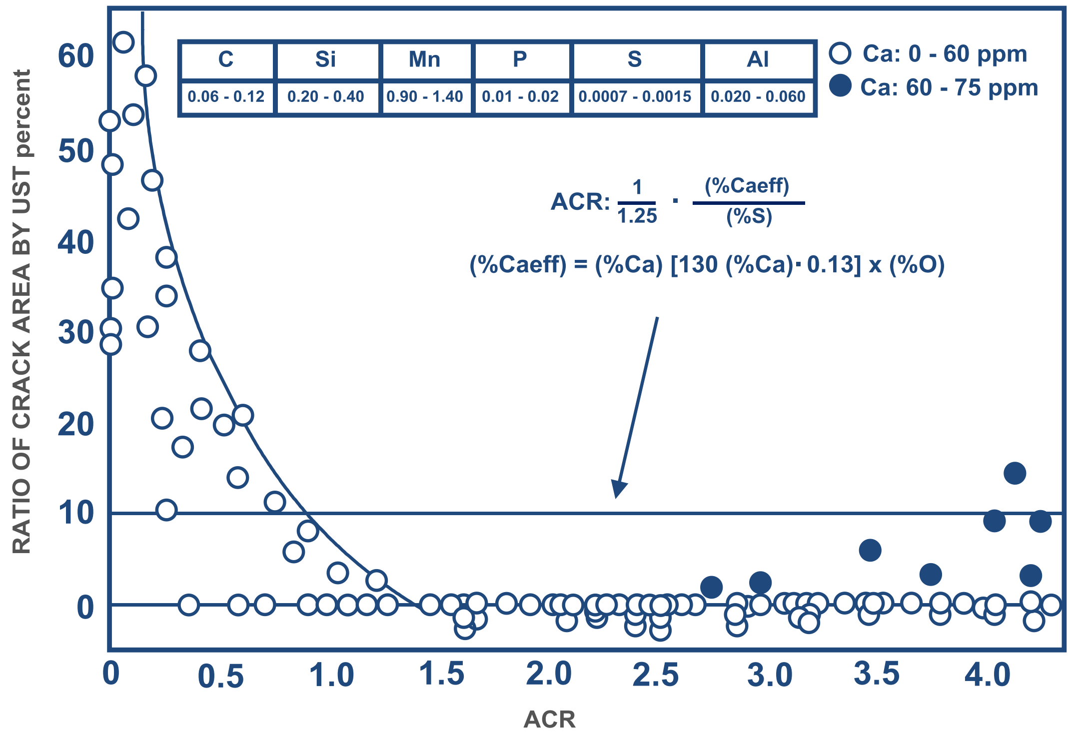


Figure 4. Relationship between ratio of crack area by UST and ACR (index of sulfide shape control) using NACE test solution [6].

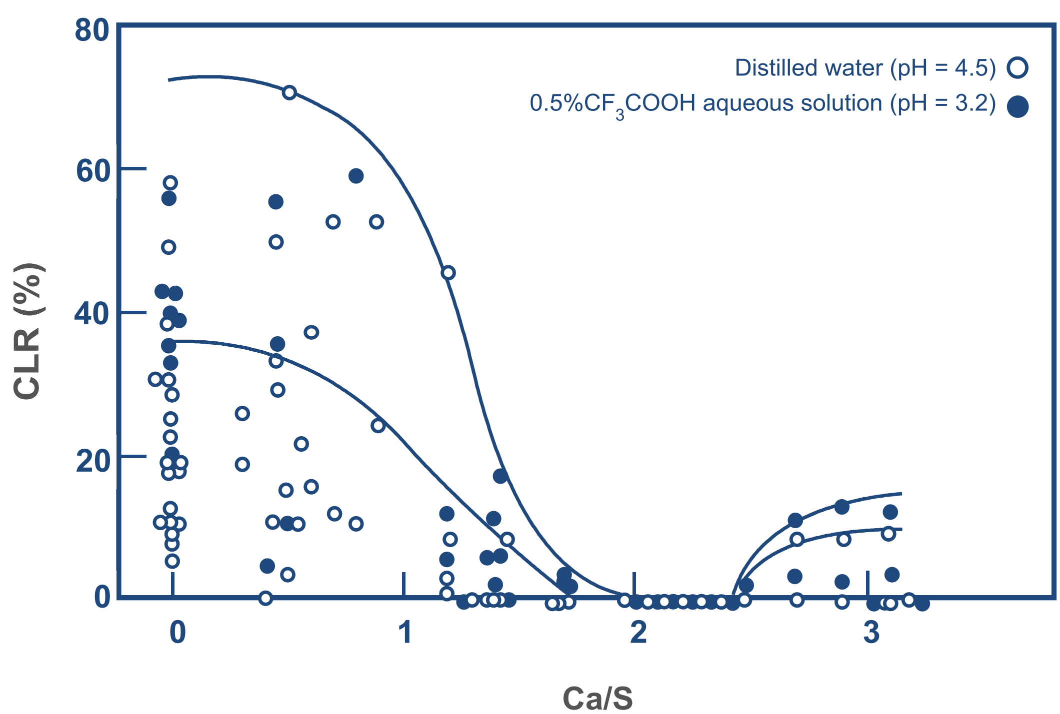


Figure 5. Effect of Ca/S ratio on crack length ratio (CLR%) [7].

Another approach for improving HIC resistance is to alloy with copper and/or chromium which produce a buffered surface layer, reducing the ingress of atomic hydrogen. These elements are most effective at moderate pH levels (>4.6) and are therefore typically used when the NACE-B, pH 5.2 solution is specified. The dramatic benefits which can accrue with copper alone are demonstrated in Figure 6.

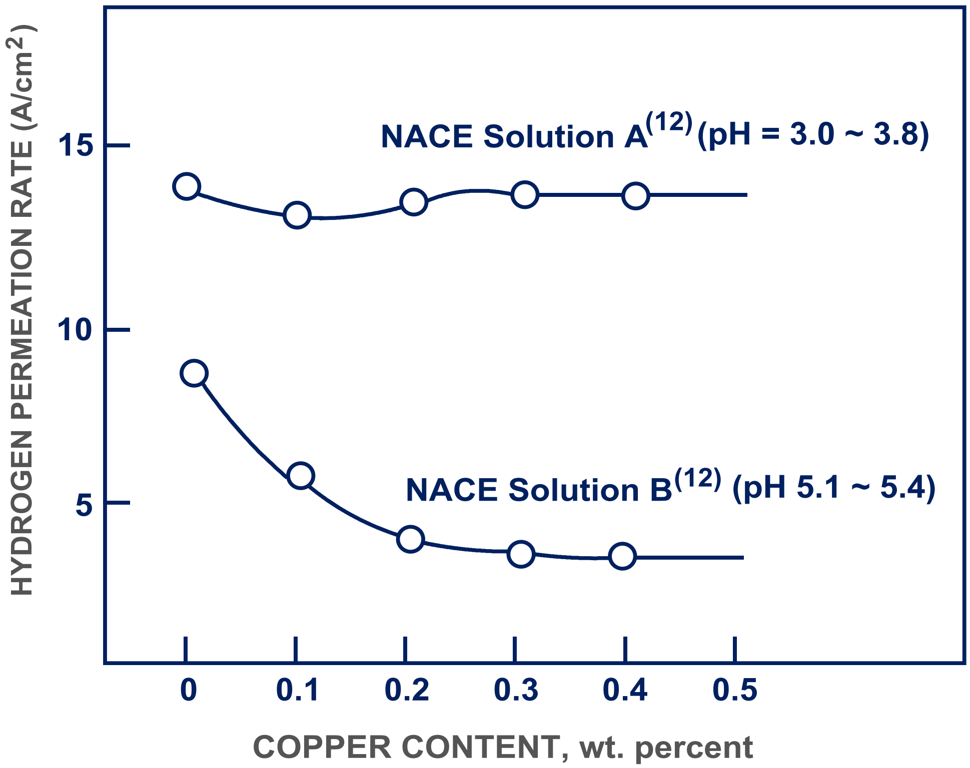


Figure 6. Effect of copper on hydrogen permeation rate for NACE TM0284 Solutions A and B [8].

Whilst copper primarily appears to be effective with the higher pH solution, it is the author's opinion that its use should always be considered even when Solution A testing is specified because in service pH levels are usually much higher than this and copper can produce benefits under upset conditions.

In practice, it can be risky to use copper on its own due to its potential to produce hot shortness during rolling and other elements such as nickel at the 0.12 to 0.15% level can be considered for use in conjunction with copper. Molybdenum additions should be specifically avoided since they destroy (poison) the effectiveness of the buffered layer and if higher strength is required a much more acceptable addition is chromium.

As shown in Figure 7, strengthening additions of chromium, when used with copper, preserve the benefits of the latter element at long exposure times as described earlier for the NACE pH 5.2 solution.

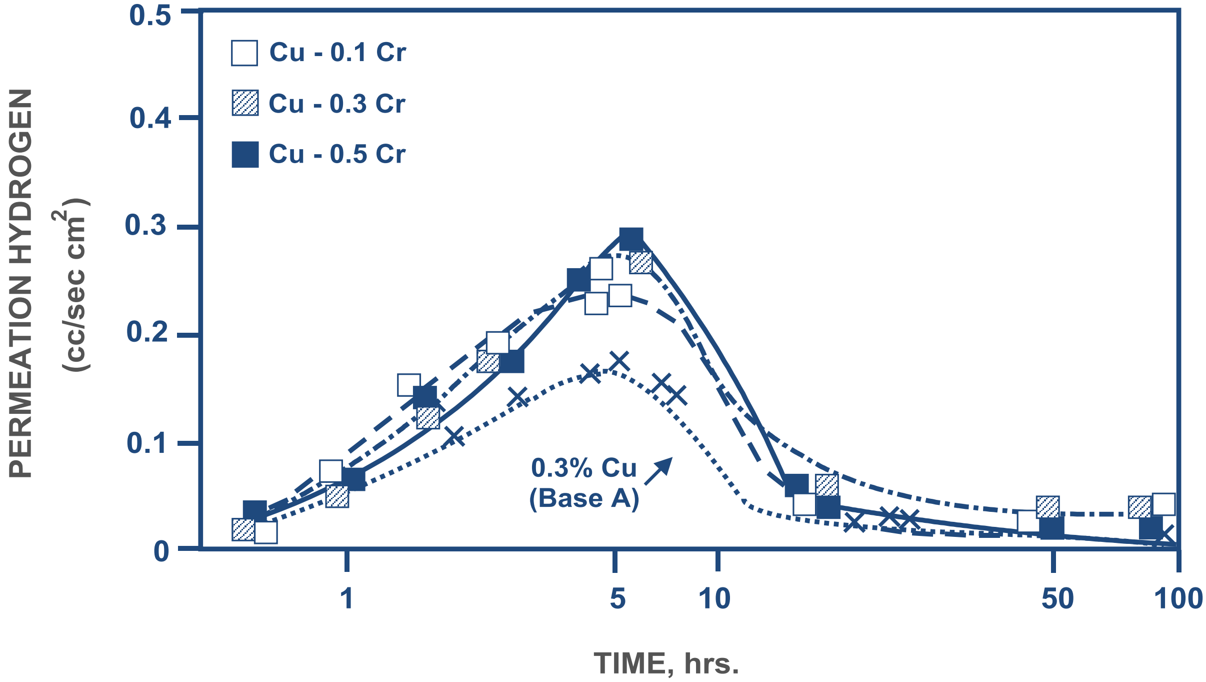


Figure 7. Effect of Cr on hydrogen permeation rates for Cu-bearing steels TM0284 Solution B (pH 5.2) [6].

Today, sour service linepipe steels generally have carbon contents below 0.06 percent and phosphorus contents below 0.015 percent or even 0.010 percent, with reduced pearlite banding and minimized tendency for centerline segregation. Thus a typical or classical X60 sour service product might have the chemical composition shown in Table IV.

Table IV. Typical Chemical Composition of X60 Sour Service Linepipe, wt.%

C	Mn	Si	S	P	Nb	Cu	Cr	Al	Ca
0.04	1.15	0.18	0.0015	0.013	0.04	0.28	0.27	0.03	0.0018

The Low Manganese Concept

This development is described in detail in U.S. Patent No. 5,993,570 dated November 30, 1999 [9]. The new steel typically has a manganese content well below 0.45 percent. The technology grew out of a need for producing sour resistant steels in older manufacturing facilities with substandard continuous casting machines or at high casting speeds associated with thin slab casters. Additionally, it has been discovered that the steel is more tolerant of residual sulfur while simultaneously performing well in the absence of adequate calcium residuals.

The reasons for this behavior are:

i. The plasticity of manganese sulfide is reduced at low Mn:S ratios such that the MnS inclusions are less elongated when present in the centerline segregated regions. This reduces reliance on complete calcium inclusion shape control;

ii. At very low manganese contents (<0.3%) Meyer *et al* [10] have shown that MnS is not stable in the presence of titanium (0.020-0.080 percent). Instead titanium sulfides or carbosulfides are formed, Figure 8, both of which are hard and refractory and remain globular during hot rolling.

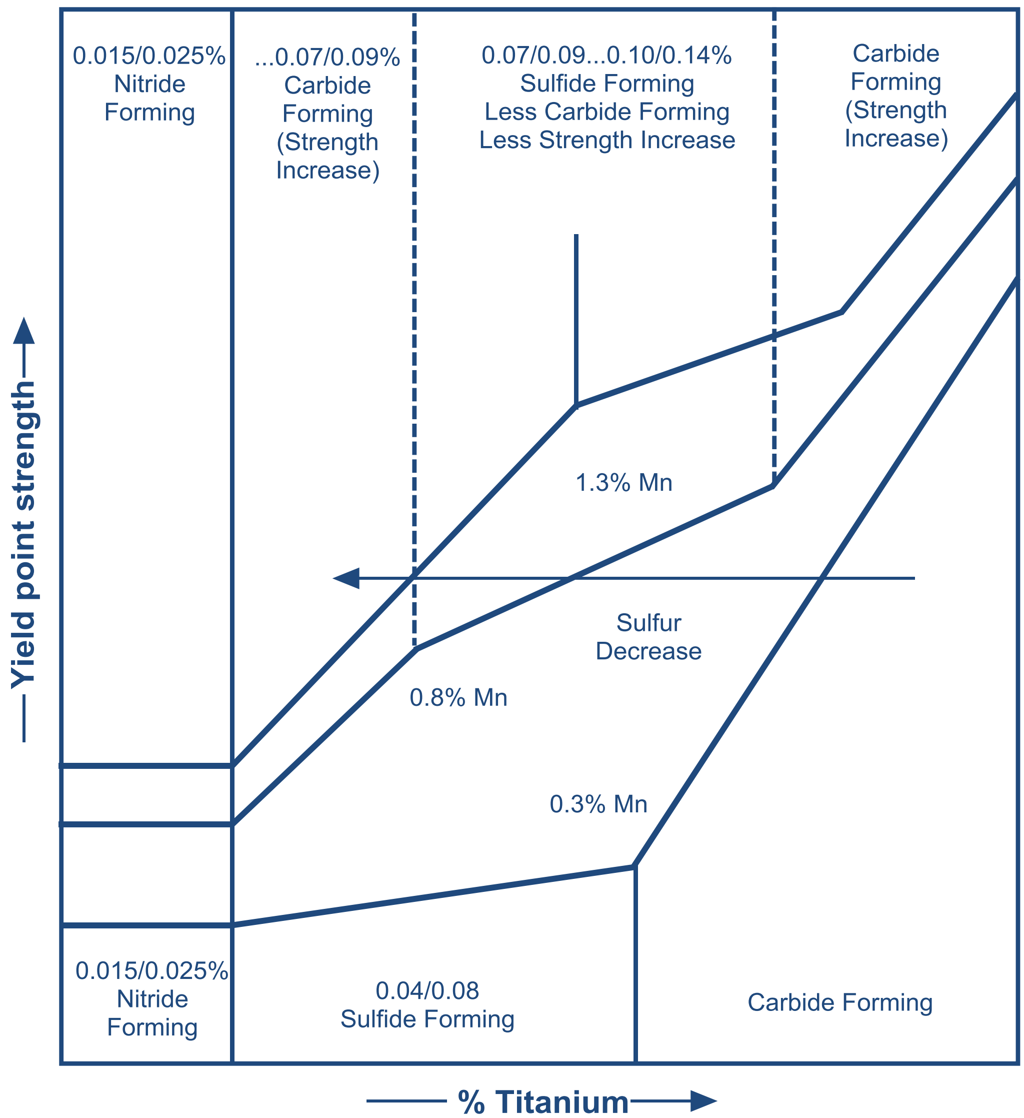


Figure 8. Schematic correlation between titanium content and yield point as a function of manganese content and also indications of the type of precipitates and their effect on hardening [10].

Compared to that of conventional steels with higher manganese, the yield strength of low manganese steels are reduced due to lower solid solution strengthening and to an increase in transformation temperature, but this is compensated by additions of chromium in the range 0.20 to 0.65 percent and the addition of greater amounts of niobium (0.065 to 0.095 percent), since both elements help reduce the $\gamma \rightarrow \alpha$ transformation temperature, while niobium provides an excellent response to high temperature austenite processing (the HTP concept). This is partly the result of a reduction in NbC solubility at low manganese contents, which thus raises the temperature of non-recrystallization T_{nr} [11,12].

The yield strengths of very low manganese steels are presented in Figure 9 [9], which shows that it is possible to readily achieve API Grade X65 properties in small diameter ERW linepipe. The toughness of the steels is considered excellent, Table V, due to the very fine grained microstructures developed during rolling at moderate to high temperatures.

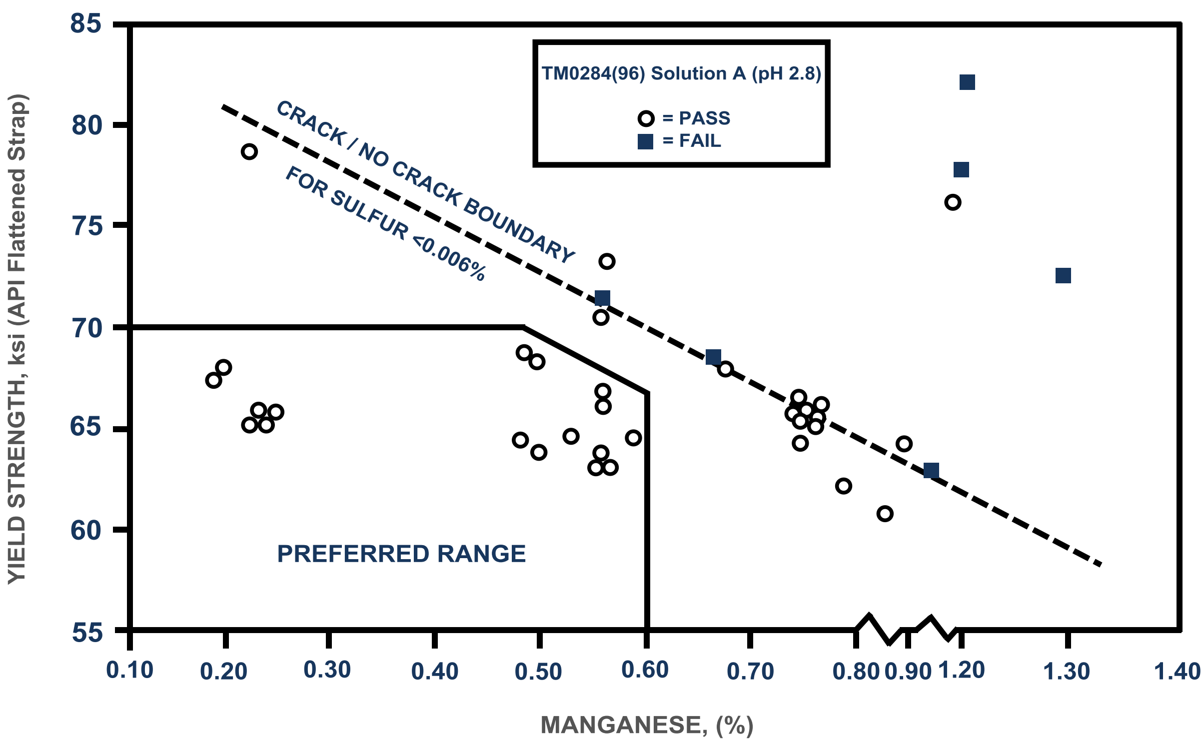


Figure 9. Stepwise cracking as a function of pipe yield strength and manganese content [9].

Table V.
(a) Chemical Composition of Production Heats, wt.%

Steel	**C**	**Mn**	**P**	**S**	**Cb(Nb)**	**Si**	**Ti**	**Cu**
A	0.046	0.230	0.005	0.004	0.054	0.210	0.013	0.250
B	0.032	0.220	0.006	0.004	0.052	0.200	0.021	0.250
C	0.045	0.190	0.005	0.004	0.048	0.160	0.011	0.000
D	0.052	0.220	0.007	0.004	0.051	0.200	0.020	0.250
Steel	**Ni**	**Mo**	**Cr**	**V**	**Al**	**B**	**Ca**	**N**
A	0.130	0.000	0.020	0.007	0.063	0.000	0.002	0.004
B	0.130	0.011	0.020	0.007	0.039	0.000	0.000	0.004
C	0.010	0.240	0.020	0.007	0.047	0.000	0.001	0.005
D	0.130	0.230	0.020	0.007	0.044	0.000	0.000	0.004

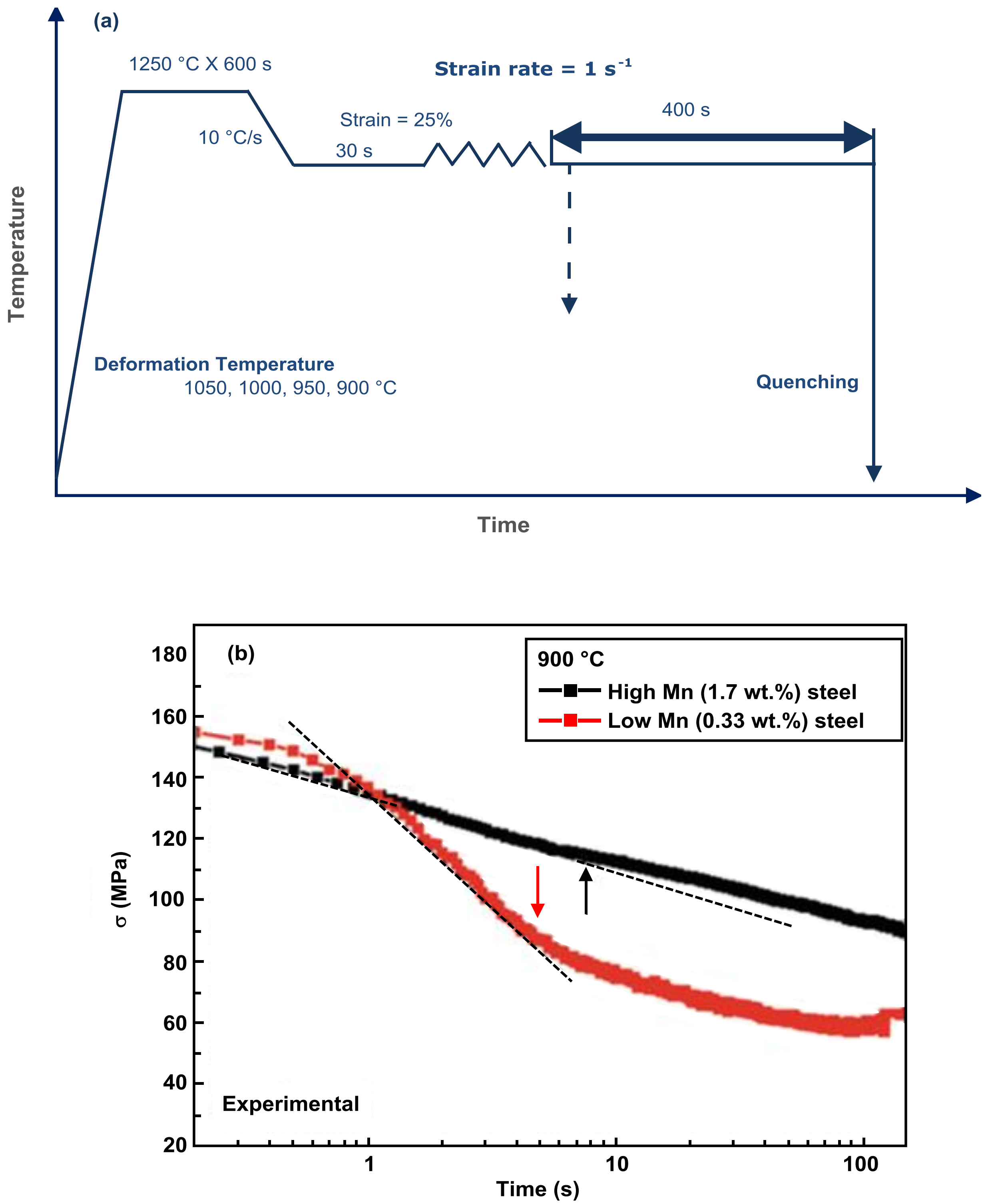
(b) Charpy Results for 9.8 mm Skelp

Energy Average (ft-lbs) 2/3 Size						
-	**32 °F**	**0 °F**	**-20 °F**	**-40 °F**	**-60 °F**	**-80 °F**
Steel A	158	128	142	101	108	76
Steel B	182	81	184	184	181	177
Steel C	161	144	130	118	92	9
Steel D	151	133	129	130	69	67
Shear Area Average (%)						
	32 °F	**0 °F**	**-20 °F**	**-40 °F**	**-60 °F**	**-80 °F**
Steel A	100	100	100	84	86	67
Steel B	100	100	100	100	100	100
Steel C	100	100	100	100	76	8
Steel D	100	100	100	92	46	40

The austenite processing response of low manganese steels is covered in excellent papers published by Subramanian *et al* [11,12]. Some of these results are presented in Figure 10.

The greatly reduced segregation tendency of manganese, at very low manganese levels, is shown in Figure 11. Since the steels solidify in the α ferrite region, where solute diffusion rates are high, segregation of other elements such as chromium and copper may also be reduced. This minimizes the inevitable segregation of carbon and phosphorus at the slab centerline.

Additional yield strength data for steels further alloyed with copper and nickel are presented in Figure 12 and Tables VI and VII [12]. It can be seen that there is a beneficial effect of these elements in maintaining strength as wall thickness increases.


(a)
Temperature
1250 °C X 600 s
10 °C/s
Strain = 25%
30 s
Strain rate = 1 s-1
400 s
Deformation Temperature
1050, 1000, 950, 900 °C
Quenching
Time
(b)
900 °C
High Mn (1.7 wt.%) steel
Low Mn (0.33 wt.%) steel
Experimental
σ (MPa)
Time (s)
180
160
140
120
100
80
60
40
20
1
10
100

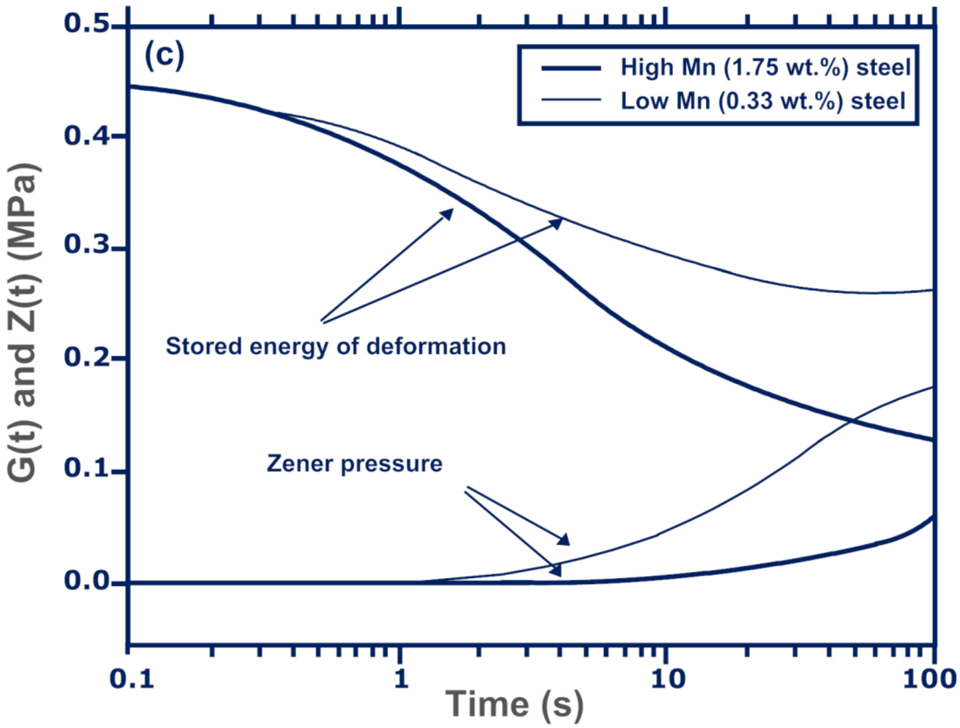


Figure 10. Results of industrial high Nb (0.09 wt.%) steel with different Mn content by stress relaxation test at 900 °C; (a) Experimental process of stress relaxation tests, (b) Stress relaxation curves of 1.75 wt.% Mn and 0.33 wt.% Mn steel, (c) Evolution curves of stored energy and Zener pressure generated by Zurob's model [11,12].

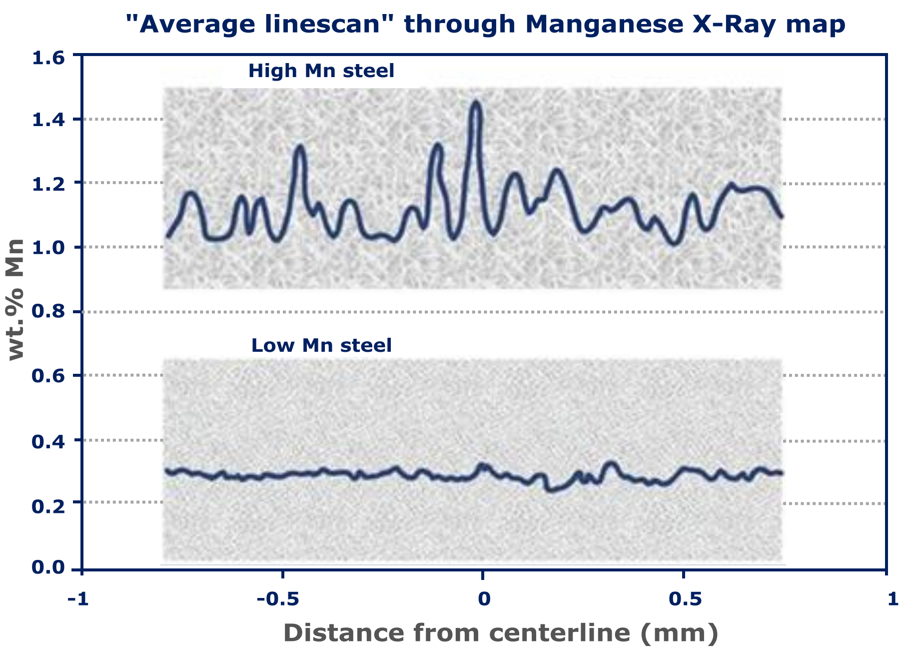


Figure 11. Low levels of segregation in low Mn steel compared with high Mn steel [13,14].

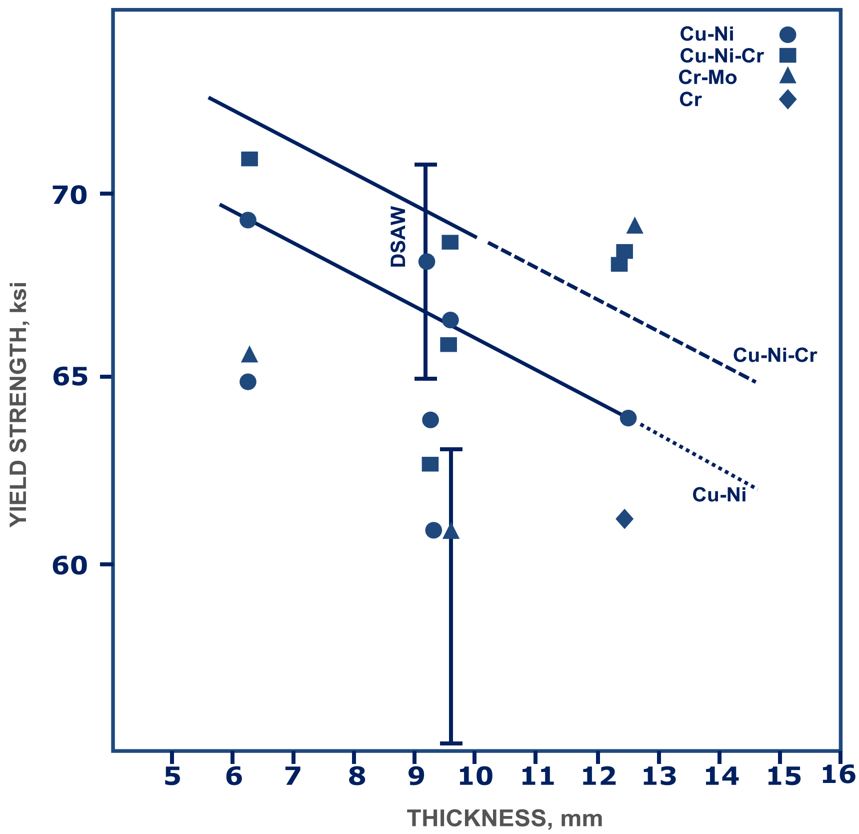


Figure 12. Yield strength as a function of skelp thickness for various alloying combinations.

Table VI. Production Data for 11.8 mm ERW Pipe;
(a) Steel Composition, wt.%, Coil Number 1

C	**Mn**	**P**	**S**	**Nb**	**Si**	**Ti**	**Cu**
0.032	0.220	0.006	0.004	0.052	0.200	0.021	0.250
Ni	**Mo**	**Cr**	**V**	**Al**	**B**	**Ca**	**N**
0.130	0.010	0.020	0.007	0.039	0.000	0.000	0.004

(b) Strength and Impact Properties of Coil Number 1

Pipe after Oven			
Yield (ksi)		**Tensile (ksi)**	
Ring	**Strap**	**P**	**W**
N/A*	66.0	71.5	72.0

Charpy											
Energy Average (ft-lbs)						**Shear Area Average (%)**					
32 °F	**0 °F**	**-20 °F**	**-40 °F**	**-60 °F**	**-80 °F**	**32 °F**	**0 °F**	**-20 °F**	**-40 °F**	**-60 °F**	**-80 °F**
182	181	184	184	181	177	100	100	100	100	100	100

N/A* = Not available
P = Pipe, W = Weld

(c) DWTT Properties of Coil Number 1

Drop Weight Tear Test						Transition Temperature °F			
Shear Area Average (%)						Charpy		DWTT	
32 °F	0 °F	-20 °F	-40 °F	-60 °F	-80 °F	50%	85%	50%	85%
100	100	100	100	100	28	<-80	<-80	-75	-65

Table VII. Production Results for 12.7 and 14.27 mm Skelp;
(a) Steel Composition, wt.%

Steel Type	%C	%Mn	%Si	%S	%P	%Al	%Cr	%Nb	%V	Others	%CE
Trial Heat 1	0.040	0.290	0.170	0.0024	0.013	0.040	0.400	0.086	0.001	Cu+Ni+ Ti+Ca	0.198
Trial Heat 2	0.035	0.240	0.175	0.0016	0.012	0.034	0.410	0.084	0.052		0.198
Conventional Heat	0.042	0.900	0.230	0.0012	0.012	0.035	0.015	0.058	0.030		0.229

(b) Mechanical Properties

Steel Type	Thickness	YS	TS	% EL	YS/TS	Hardness	CVN Impact Energy (J) at 0 °C				DWTT
	mm	MPa	MPa			HV10	1	2	3	Avg	%SA
Trial Heat 1	12.70	432	481	39	0.898	189	238	232	227	232	>95%
Trial Heat 2	14.27	448	498	34	0.899	192	216	224	218	219	>95%
Conventional Heat	14.27	449	500	35	0.898	194	240	237	260	246	>95%

(c) HIC Results ANSI-NACE TM0284 Solution A

Steel Type	Thickness	HIC Test Results			
	mm	CTR	CLR	CSR	Remarks
Trial Heat 1	12.70	0.00	0.00	0.00	Satisfactory
Trial Heat 2	14.27	0.00	0.00	0.00	Satisfactory
Conventional Heat	14.27	0.00	0.00	0.00	Satisfactory

At the present time, CBMM is in the process of producing trial slabs with the chemical composition shown in Table VIII.

Table VIII. Chemical Composition of Trial Slabs, wt.%

	C	Mn	S	P	Nb	Ti	Cr	Cu	Ni	Ca	Al	N
Max.	0.055	0.30	0.003	0.015	0.095	0.015	0.55	0.32	0.20	0.0025	0.035	0.008
Aim	0.045	0.25	0.0015	LAP*	0.085	0.011	0.45	0.29	0.15	0.0015	0.025	LAP*
Min.	0.035	0.20	None	None	0.075	0.007	0.40	0.26	0.12	0.0010	0.020	None

LAP* - low as possible

The slabs will be distributed to several mills for rolling and pipe making and further evaluation using HIC, SOHIC and SSC test methods.

Conclusions

Sour service linepipe steels have evolved significantly since the unfortunate failure in a BP pipeline in 1972 in the Umshaif (Arabian) Gulf.

Carbon, manganese, sulfur and phosphorus levels have been reduced and hot rolling practices have been improved by moving to higher finishing temperatures. The steels are usually calcium treated for inclusion shape control and often alloyed with 0.24 to 0.30 percent copper. Until recently, manganese contents around 0.90-1.20 percent have been typical, but further improvements in HIC resistance can be achieved at extremely low manganese contents of 0.20-0.45 percent. Such steels have been shown to be more tolerant of higher residual sulfur contents (0.003-0.005 percent) even if calcium treatment is not perfect.

This is the result of reduced MnS plasticity and the thermodynamic potential for formation of globular titanium carbo-sulfide particles at low manganese levels.

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