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research report

Identification of Commercially Available Alloys for Corrosion-Resistant Metallic Reinforcement and Test Methods for Evaluating Corrosion-Resistant Reinforcement

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16. Abstract

A literature review was conducted with the goal of identifying alternative low-cost corrosion-resistant steel reinforcement materials. The most promising alternate reinforcing materials seen to date that are less expensive than 300 series stainless steels include low-nickel austenitic stainless steels and a variety of ferritic or martensitic 12-15 weight percent chromium steels. Steels with 2.5-10 weight percent chromium may also be of interest because they offer a marginal gain in corrosion performance at a very low cost. Several steel types that should undergo further evaluation are 201LN, 216, Duracorr, Enduramet 32 and Enduramet 33, HSS2, Lapealloy, S41425, S41426, and S42300.

Corrosion-resistant steels are alloyed to ensure the steel itself has sufficient corrosion protection qualities; therefore, it is sensitive to cost fluctuations in raw materials. Based on the last 7 years, bars with higher nickel and molybdenum contents are sensitive to the cost of these alloying elements, whereas bars with higher chromium contents have been only slightly sensitive to the raw material cost. The cost of alloying materials also reflects the cost of different types of stainless steels. Both martensitic and ferritic stainless steels demonstrated slight increases in the average surcharge over a 7-year period, whereas austenitic, duplex, and precipitation hardening stainless steels increased dramatically.

The most promising test for determining chloride threshold (initiation) in the laboratory is the +100 mV vs. SCE (or +200 mV vs. SCE) potentiostatic hold. The Cl^- threshold can be established for the new rebar materials by conducting potentiostatic holds at +100 mV vs. SCE at various fixed Cl^- levels. This method can also be extended to mortar-covered bars immersed in a simulated pore water solution with a thin mortar layer thickness. Propagation tests can also be conducted by conducting either potentiostatic holds at selected potentials or galvanic coupling in a split cell. A propagation law and repassivation potential (i.e., a "no propagation threshold" threshold potential) can be established. Concerning field testing, the ASTM G109 method is recommended primarily for comparison to existing research data. This test can be used to assess Cl^- thresholds either by varying Cl^- levels in the mortar mix or core drilling/sampling. Initial recording of galvanic current indicates initiation, whereas spalling provides an engineering indication of propagation. The Florida Department of Transportation's tombstone method should also be considered as a variation of the ASTM G109 method in high-permeable/low-permeable concrete mixes in order to test candidate rebar in concrete. ASTM G109 and Florida Department of Transportation tombstone concrete specimens can be artificially cracked to accelerate the onset of corrosion.

Finally, the mechanical properties for each steel will need to be determined. Data will need to be gathered on specimens that have been rolled to the final reinforcing steel dimensions, although some of the bars identified could potentially function in the same capacity as the MMFX-2. However, additional research is required for the higher strength steels for structurally critical areas.

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FINAL REPORT

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Finally, the mechanical properties for each steel will need to be determined. Data will need to be gathered on specimens that have been rolled to the final reinforcing steel dimensions, although some of the bars identified could potentially function in the same capacity as the MMFX-2. However, additional research is required for the higher strength steels for structurally critical areas.

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INTRODUCTION

Alloying of ferrous metals to enhance certain desirable characteristics has a long history. In broad terms, the effect of material composition in ferrous alloys is well understood.[1, 2] The low carbon content improves the welding properties of the alloy and provides improved resistance to pitting and general corrosion as a consequence of reduced chromium carbide ($Cr_{23}C_6$) formation and associated chromium (Cr) depletion. Nickel (Ni) is known to be an austenite stabilizing element. In 13% Cr low carbon alloys, Ni is used to obtain a fully austenitic material during hot working and then a fully martensitic material without any delta ferrite phase after quenching.[3] Another reason Ni is added is to compensate for the reduced hot workability associated with the introduction of molybdenum (Mo) and lowered carbon (C) and nitrogen (N). Manganese (Mn) and copper (Cu) also are austenite stabilizers, whereas Cr and silicon (Si) favor ferrite formation.[4] The addition of Cr and Mo improves pitting resistance and enhances passivity. This improvement can occur due to a combination of producing a more resistant passive film by providing better coverage/connectivity of the protective layer, reducing the anodic peak making the transition from active to passive behavior easier, and reducing the dissolution rate for material at local corrosion sites making sustaining the local chemistry necessary for localized corrosion more difficult. Nitrogen has a complex synergistic effect in iron (Fe)-Cr-Mo alloys that produces a potent effect in practice, but is not mechanistically well understood

In recent years, several literature reviews have been published regarding alternate reinforcing bars (rebars) containing many of these elements. From an earlier review by

McDonald et al.[5, 6] to more recent reviews by Hurley,[7] Hartt et al.,[8] and Nürnberger,[9] the findings, in general, advocate the use of descaled austenitic and duplex stainless steel (≥18% Cr and ≥ 8% Ni) because of their higher pitting resistance equivalency number (PREN). The Virginia Transportation Research Council (VTRC) has sponsored several research projects to test some alternate rebars.[7, 10-18] These tests were conducted on samples in solution[7, 10, 15-18] and embedded in concrete.[11-14] A recent project[10] investigated the chloride threshold concentrations for solid 316LN stainless steel (UNS S31653), 316L stainless steel clad, 2101 LDX duplex stainless steel (UNS S32101), MMFX-2 (ASTM A1035), and carbon steel (ASTM A615) rebars through laboratory tests in saturated calcium hydroxide ($Ca(OH)_2$) plus sodium chloride (NaCl) solutions. From these tests, it was found that a solid 316LN stainless steel rebar in a chemically pickled condition has a much higher chloride threshold than is specified in ASTM A615. The chloride threshold was expressed as the ratio of chloride ion (Cl^-) to hydroxide ion (OH^-) concentrations in molarity. This ratio was used instead of mass of Cl^- per unit volume concrete (lb Cl^-/yd^3 concrete), which is typically used for tests conducted in concrete slabs. The 316LN (i.e., threshold Cl^-/OH^- ratio > 20) had a chloride threshold much greater than that of carbon steel ($0.25 < Cl^-/OH^- < 0.34$). Pickled 2101 LDX had a chloride threshold Cl^-/OH^- ratio of 9.7, and un-aged pickled MMFX-2 had a chloride threshold Cl^-/OH^- ratio of 4.9. 316L stainless steel clad rebar had a chloride threshold Cl^-/OH^- ratio of 4.9 with intact cladding. Stainless steel clad rebar materials in theory offer the corrosion resistance of solid stainless steel, but in practice, they usually suffer from a defect such as a cut or poorly welded cut end cap end that lowers the Cl^- threshold in laboratory potentiostatic testing. Detrimental corrosion behavior brought about by this condition is not necessarily detected during ASTM G109 testing.[11, 12]

The use of ferritic stainless steels has been suggested for mild environments (where the aggressive agent is carbonation only).[9] Two other steel alloys[8, 10, 19-21] that have been studied are MMFX-2 (which usually contains ~9.5% Cr) and 3Cr12 (10%-12% Cr), which are below the Cr composition considered necessary to form a stainless steel. The required Cr level for a stainless steel is controversial but is often quoted at 13% Cr. Nürnberger[9] indicated that if a concrete reinforced steel structure is exposed to marine environment, the recommended alloy is a Type 316 alloy stabilized with titanium[22] (UNS S31635/EN 1.4571) or an alloy that is more corrosion resistant than UNS S31635. Depending on how aggressive the exposure environment is, the corresponding corrosion resistant alloy is, e.g., a structure exposed in a mild environment, an alloy UNS S40800 (EN 1.4003), which is a standard ferritic grade stainless steel, is recommended. UNS S40800 is less corrosion resistant than UNS31635.

A research group in Japan[23-25] has evaluated several Fe-Cr alloys with various Cr% levels as possible rebars. Table 1 shows the compositions investigated by this group. The PREN values for these alloys, which are based on the compositions shown in Table 1, are reported in Table 2.

It appears that alloys with Cr ≥ 13% could perform adequately in mild to medium aggressive environments up to 4.0 lb/yd^3 (2.4 kg Cl^-/m^3). Alloys with 16% Cr performed the best in concrete with up to 40 lb/yd^3 (24 kg/m^3) of chlorides admixed, as only a small amount of corrosion was observed after their forensic analysis.[23-25] It is not clear if any of these steels are being produced as reinforcing steel. McCafferty[26] suggested that 12% Cr is needed in order to have a good passive layer. However, primary passivity may be observed at as low as 10% Cr

Table 1. Alloys Investigated in Research Program in Japan and Similar Products[25]

Alloys	Nearest Equivalent	%								
		Cr	C	Si	Mo	Mn	P	S	Ni	N
SD345	ASTM A615	0.08	0.228	0.31	0.016	1.34	0.029	0.02	0.04	0.005
0Cr	UNS G10080	0.01	0.012	0.32	0.001	0.5	0.031	0.006	0.01	0.010
5Cr	ASTM A387–5	5.02	0.015	0.28	0.001	0.53	0.027	0.006	0.01	0.006
9Cr	ASTM A387–9	9.14	0.011	0.28	0.001	0.53	0.028	0.006	0.01	0.010
11Cr	UNS S40300[a]	11.00	0.012	0.28	0.001	0.53	0.028	0.004	0.01	0.010
13Cr	UNS S40500	13.05	0.012	0.28	0.002	0.53	0.028	0.004	0.01	0.008
16Cr	UNS S42900	15.98	0.011	0.29	0.002	0.53	0.027	0.004	0.01	0.009
SUS304	UNS S30400	18.36	0.063	0.31	0.053	1.01	0.026	0.006	8.28	0.046

[a] Nearest equivalent is a stainless steel; however, the chromium percentage in this alloy is below the value for stainless steel.

Table 2. Calculated PRENs for Alloys Investigated in Research Program in Japan

Alloy	PREN
SD345	0.14
0Cr	0.01
5Cr	5.0
9Cr	9.1
11Cr	11.0
13Cr	13.1
16Cr	16.0
SUS304	18.5

PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 1.

(onset of Cr passivation), and up to 17% Cr was recently stated to be the level necessary to produce a continuous Cr-rich oxide film.[27] A 13% Cr level was reasoned to be a reactivation threshold for depassivation of the steel in a strong reducing acid.[28] Without consideration of the effects from other elements, it would appear that alloys with Cr should be considered and those with Cr > 12 % should be strongly considered were chloride laden environment exist.

The literature shows that considerable highway research work has focused on mitigating corrosion in reinforced concrete structures. As previously discussed, a portion of this research investigated the use of alloying to improve the corrosion resistance of reinforcing steel, which resulted in the actual production of corrosion-resistant reinforcement (CRR). Table 3 provides a list of the currently manufactured CRR materials and the alloy composition of each bar type. Unfortunately, some steels are sensitive to the cost of certain alloying elements, which can increase the overall construction cost when compared to the former incumbent epoxy-coated rebar (ECR).

PURPOSE AND SCOPE

The purpose of this study was (1) to identify a small group of commercially available steels that are corrosion resistant and have the potential for use as a low-cost alternative to the currently accepted CRR in Virginia bridge decks and should be considered for subsequent

Table 3. Currently Available Carbon Steel and Corrosion-Resistant Reinforcement Alloy Compositions

Common Name	Steel Type	UNS	Nearest Equivalent	Composition (wt. %)									Reference No.
				Cr	Ni	Mo	N	C	Mn	Si	S	P	
Typical carbon steel[a]	Ferritic-pearlitic carbon steel	ASTM A615	SD345	0.150	0.097	0.018	0.012	0.440	1.260	0.230	0.029	0.010	10, 29
MMFX-2	Austenitic-martensitic alloyed steel	ASTM A1035	---	8.0 – 10.0	---	---	0.05	0.15	1.5	0.045	0.045	0.035	10, 30
EnduraMet 2205	Ferritic-austenitic (duplex) stainless steel	S31803	EN 1.4462, SUS 329J3L	21.0-23.0	4.5-6.5	2.5-3.5	0.08-0.20	0.03	2.00	1.00	0.020	0.030	31-34
EnduraMet 32	Austenitic stainless steel	S24100	Nitronic 32 (18-2-Mn)	16.5-19.0	0.05-2.50	---	0.20-0.45	0.06	11.0- 14.0	1.00	0.030	0.060	31, 35
EnduraMet 33	Austenitic stainless steel	S24000	Nitronic 33 (18-3-Mn)	17.0-19.0	2.50-3.75	---	0.20-0.40	0.08	11.5- 14.5	1.00	0.030	0.060	31, 36
304	Austenitic stainless steel	S30400	EN 1.4301, SS_{14} 2332, SUS 304	18.00-20.00	8.00-10.50	---	0.10	0.08	2.00	1.00	0.030	0.045	31, 34, 37
316 L	Austenitic stainless steel	S31603	EN 1.4404, SS_{14} 2348,	16.0-18.0	10.0-14.0	2.0-3.0	---	0.03	2.00	1.00	0.03	0.045	31, 37
316 LN	Austenitic stainless steel	S31653	DIN 1.4429	16.0-18.0	10.0-14.0	2.0-3.0	0.10-0.16	0.03	2.00	1.00	0.03	0.045	31, 33, 37
Clad Bar 304[b]	Carbon steel core with an austenitic cladding	S30400	EN 1.4301, SS_{14} 2332, SUS 304	18.00-20.00	8.00-10.50	---	0.10	0.08	2.00	1.00	0.030	0.045	34, 37
Clad Bar 316	Carbon steel core with austenitic cladding	S31600	EN 1.4401, SS_{14} 2347, SUS 316	16.0-18.0	10.0-14.0	2.0-3.0	---	0.08	2.00	1.00	0.03	0.045	34, 37

Values are a maximum unless indicated, and the unlisted balance is iron. UNS = Unified Numbering System.
[a] Plus Cu.

evaluation in the laboratory and field and (2) to determine which test methods would be best suited for evaluating future CRR bars. It was anticipated that this research would support the needs of VDOT as it eliminates the use of ECR in bridge decks and phases in the use of CRR for bridge deck construction.

The criteria chosen for evaluation of the alloys were corrosion resistance, mechanical properties, and cost. The criteria chosen for test selection were tests that evaluate the corrosion resistance behavior during the initiation and propagation stages, as well as tests that evaluate the mechanical properties.

This report uses abbreviations that are commonly used in materials science and engineering. A description of each abbreviation is provided in Appendix A.

METHODOLOGY

Overview

Two tasks were undertaken to achieve the study objectives:

1. *A group of commercially available steels were identified that fulfilled the following criteria:*

   - strong corrosion resistance attributes
   - mechanical properties that were similar to those of carbon steel rebar
   - low material cost

   In addition to these criteria, the steels had to comply with the “Buy America” requirements under 23 CFR 635.410, which apply to all federal-aid highway construction projects. The following points in particular had to be considered:[38, 39]

   - The requirements pertain to iron and steel products.
   - All manufacturing processes for steel or iron materials must occur in the United States.
   - Manufacturing is considered to be from the initial melting of the iron or steel to the final finishing stage.
   - The supply of raw material does not need to be domestic.

   To identify these steels, a literature review was initially conducted and then subsequent discussions via email or telephone calls with various steel manufacturers and steel trade organizations were held. The literature was identified through the use of various online databases that were available through the University of Virginia, Florida Atlantic University, and Virginia Department of Transportation Libraries. The manufacturers and trade organizations were selected based on evaluating if these orgainations had involvement with the steel alloys that were identified during the literature review.

2. *A determination was made regarding the test methods that would be best suited for evaluating future CRR bars.* A literature review of the various corrosion related tests was done. The literature was reviewed through the use of various online databases that were available through the University of Virginia, Florida Atlantic University, and the VDOT Research Library. In addition, discussions with structural engineers at the VTRC provided insight as to which mechanical test should be included.

Identification of Steels

In this report, all alloy compositions are given as weight percentages (wt.%) except when noted. To identify alloys, when possible, the Unified Numbering System (UNS) was used.

Desired Corrosion Resistance Attributes

Most alloys discussed in the following sections were developed with objectives other than to function as reinforcing steel. Thus, minimal information is available on how they would perform in alkaline environments and what their Cl^- threshold might be in such solutions. The majority are high-strength steels that are used in a variety of industrial applications. Moreover, the pitting resistance equivalency number (PREN) has been only marginally successful in predicting the corrosion resistance in concrete according to several investigators despite its widespread success in aqueous solutions containing Cl^-.[7, 8, 10, 20, 21, 40, 41]

The PREN is often given by:

$$\text{PREN} = \%\text{Cr} + 3.3 * \%\text{Mo} + 16 * \%\text{N}$$

where

%Cr = wt.% chromium
%Mo = wt.% molybdenum
%N = wt.% nitrogen.

Some individuals, however, have used a number of 30 instead of 16 in the last term in recognition of the extremely beneficial effects of alloyed nitrogen.[42] However, the negative effects of undesirable constituents, such as inclusions, are generally not included in the PREN values published and therefore consideration of their influence should be taken when using these values.[43] It should be emphasized again that a monotonic correlation between the Cl^- threshold and PREN has not necessarily been observed in studies in concrete or concrete pore water solutions.[8, 10] For instance, the Cl^- threshold in simulated concrete pore solution increases somewhat for 9% Cr alloys but increases significantly for 316LN stainless steel.[7, 10]

Alloys with Cr were found to have a lower cathodic oxygen reduction reaction rate, which might limit the cathodic capacity surrounding an active corrosion site.[44] However, there is very limited published information regarding this issue, and this property might also need to be investigated for the recommended alloys derived from this study as well as for some of the steels already in use.

Therefore, the candidate materials were identified from commercially available ferrous materials (with priority for the ones available in bar form). Materials in their experimental or developmental phase were also assessed based on the literature. The identified materials complied with one or more of the desired attributes for improving the corrosion resistance of the reinforcement. The following is a list of four of the desired attributes based on corrosion resistance.

1. *Has a high Cl^- threshold.* This feature will increase the time to initiation of corrosion. The impact of mill scale on corrosion initiation is also important because mill scale has been shown to affect adversely the corrosion performance of high chromium (Cr) candidate rebar materials that undergo surface Cr depletion during scale formation.[1] A high Cl^- threshold can be related to a high PREN based on Cr, Mo, N, and tungsten (W); alloying contents; chemical descaling to restore surface Cr levels; and absence of microstructural defects.

2. *Promotes a slow oxygen reduction reaction (ORR) rate.* This will likely limit the corrosion rate, which is coupled to this reduction reaction on the reinforcement and thus, the ability to sustain propagation of the local anodes once corrosion initiates. This attribute relates to the iron (Fe), nickel (Ni), and Cr contents of the candidate steel and its microstructure. Relative to Fe, Ni and carbide metallurgical phases increase the ORR rate whereas Cr in solid solution decreases it.

3. *Forms very small anodes as it corrodes.* This is observed in stainless steel because the resulting critical corrosion depth to cause oxide-induced damage to concrete, x_{crit} (this is a measure often referred to when determining the propagation time), is then increased. This is because the depth of corrosion, x, and lateral length of corrosion, L, combine to determine whether oxide-induced spalling of the concrete cover occurs. According to one model,[45, 46] decreases in L increase x_{crit}, the critical depth of bar material that must be converted to oxide before oxide spalling occurs. Thus, materials that corrode by forming small separated corrosion sites over the reinforcing bar (i.e., small L) will require large x_{crit} values. Passivated rebar materials with high Cr, Ni, and N contents will likely experience a change in corrosion mode from general corrosion with large L values to pitting corrosion with small L values.

4. *Generates corrosion product with an oxide volume similar to the oxide molar volume of the bulk material.* If the oxide molar volume of the corrosion products is similar to the original volume of the bulk material, the propagation time will be extended. This is because a larger amount of corrosion product would be required to convert the candidate rebar to enough oxide to exert a large enough stress to spall covering concrete. Previous work[7] has shown that the theoretical molar volumes of the oxides

formed on Fe-Cr and Fe-Ni-Cr rebar materials are not substantially different than those of oxides formed on carbon steel rebar.

Desired Mechanical Properties

Many of the physical requirements desired in reinforcing steel relate to the properties of the concrete, since the concrete and steel must work together as a unit. To determine acceptable physical characteristics of the steel, one value, known as f_c', is determined from the compressive strength of a concrete cylinder that has cured 28 days. This becomes extremely important in certain areas of a structure where it is important for the rebar to yield prior to the concrete failing under compression. This design feature ensures that the structural component will fail in a ductile fashion, as the steel yields, rather than in a brittle manner if the concrete fails before the steel yields. This is not to say that bridge owners using CRR will not benefit from the higher yield strengths over traditional bars. It is possible that in the future, additional construction cost savings and a reduction in reinforcement congestion will be realized as designs are changed to use smaller diameter bars while maintaining sufficient rebar/concrete contact area. However, this study did not explore the influence these changes would have on a structure.

Mechanical properties of interest include the yield and tensile strength, fracture toughness, and fatigue endurance limit. However, similar to the bend test results, the information on other mechanical properties is limited and therefore, the reported mechanical property values are based on the current steel forms produced. In addition to tests in accordance with current American Association of State Highway and Transportation Officials (AASHTO) and ASTM International (ASTM) standards, additional fatigue tests might be needed. For this study, the correlation of fatigue endurance limit with tensile strength was used to estimate a value. The fatigue endurance limit of fatigue strength without environmental degradation is often taken as one-half to one-fourth of the tensile strength of ferrous materials.

Another important feature is that the rebar must exhibit sufficient ductility so it can be formed into the required shape. A bend test is used to assess if a rebar specimen of a particular size can withstand being bent without cracking. The steels being evaluated in this study, unfortunately, are generally not manufactured as reinforcement. Therefore, this limits what is available, including bend test results.

Cost Considerations

CRR relies on the use of alloying elements to improve the corrosion resistance of the steel. These same alloying elements can range in cost, often attributable to the availability of the element. Therefore, to offset cost fluctuations in raw materials, a surcharge can be added that reflects the higher prices the steel producer is paying. The surcharge can include the prices associated with iron and various alloying elements, such as chromium, copper, manganese, molybdenum, nickel, and titanium. In addition, a surcharge can include the cost associated with energy prices. It is important to recognize, however, that a surcharge does not necessarily reflect an increase in the cost of the final product. A manufacturer can elect to absorb these costs or pass them on to the consumer. Therefore, it is important to remember the surcharge reflects only raw material costs and not final product cost. Therefore, the surcharge can indicate the volatility of the raw materials that are used to create a product. The average surcharge value will be used as a measure of how sensitive austenitic, martensitic, ferritic, duplex, and precipitation-hardened stainless steels are to the cost of chromium, molybdenum, and nickel.

Identification of Corrosion Test Methods for Evaluating New Reinforcing Materials

Successful corrosion test methods will provide a relatively quick indication of the materials corrosion resistance. This is challenging since a candidate bar must be evaluated and accepted or rejected within a short period (less than two years), and yet it must last in a structure for up to 100 years. Therefore, various laboratory electrochemical test methods and embedded concrete slab studies were evaluated. Tests were evaluated based on if the corrosion test evaluated behavior during the initiation and/or propagation stages. Test were also evaluated based on if they were performed over a short time period, which includes many of the electrochemical methods like open circuit potential (OCP), polarization resistance (R_p), and potentiostatic measurement of chloride threshold, or if they required longer time periods like many of concrete test with embedded reinforcement, like the ASTM G109 or the Florida Department of Transportation (FDOT) tombstones methods. Finally, the authors experience with corrosion testing was used to determine which methods would be best suited for routine evaluation of candidate reinforcing bars.

RESULTS AND DISCUSSION

Identified CRR Materials

As a result of the recent high price of Ni (since 2000), several of the on-going research efforts have focused on the evaluation of stainless steel of the 200 family, as well as some modified ferritic stainless steels from the 400 family. This shift to the 200 series has taken place in the general metal market, and to some degree it has extended to rebar corrosion-resistant alloys alternatives.

Corrosion Resistance

Overview

As part of the literature review, several steels were considered, including weathering steel, low Cr alloys (1.5%-5% Cr), high (7%-13%) Cr martensitic transformable steels (containing small additions of Mo, tungsten [W], vanadium [V], N, Niobium ([Nb], and other elements), and so-called stainless steels with >15% Cr (ferritic, austenitic, or duplex). The 7%-13% Cr alloys are usually divided in nominal 9% and 12% Cr. The nominal 12% Cr section also includes some of the new low Cr stainless steels. Thus, each of the following five groups of steels is discussed with regard to corrosion resistance:

1. low alloy and weathering steels

2. 1% to 5% chromium steel alloys.
3. 7% to 12 % chromium martensitic steel alloys
4. 12% to 15% chromium steel alloys
5. low-nickel stainless steels (>15% chromium).

Materials Investigated

Low Alloy and Weathering Steels. Weathering steels are low alloy steels as specified in ASTM A242 and ASTM A588 with the compositions as summarized in Table 4. Weathering steels derive their corrosion resistance from small additions of alloying elements in the <1% to several percent range. The PRENs of these alloys will be only slightly better than carbon steel (ASTM A615M) (PREN=~0.563) owing to a slightly higher Cr content. The corrosion mitigation due to minor alloying is large in sea air and alternate wet/dry conditions but marginal in continuous immersion. Cu and Ni from <1% up to 2% or 3.75% are beneficial in alternate immersion.[47] On weathering steel, the drying process after night-time condensation produces a less porous protective oxide with alloyed Cu or Ni or Cr, increasing the tenacity and protectiveness of oxides. One study[48] on the corrosion resistance of low alloy steels in the atmosphere found that Mn, P, Si, Mo, Cu, and aluminum (Al) were beneficial additions, whereas the splash zone favored Mn, P, Mo, Al, Cu and full immersion favored Mn, Mo, Al, and Cr. However, a Cr-free weathering steel developed in Japan is said to perform better than COR-TEN B or C.[49] Finally, alloying sulfur is reported to be detrimental regarding corrosion of weathering steels.

Although many studies of weathering steel did not consider corrosion in concrete, one study in concrete[51] assessed 0.2C-0.2Si-0.40Mn-0.08W-0.04Al steels with 0.5% to 4% additions of unidentified elements A, B, and C. The corrosion results in concrete showed one-half to one-third of the corrosion expressed as milligrams per 100 grams as seen in unalloyed steel after 12-month tests. Chowdhury[52] criticized the use of weathering steels in concrete, lamenting that Cr will provoke more dangerous pitting and crevice attack compared to low alloy steels. However, pitting with lack of lateral corrosion on a bar was shown by Sagüés[53] to be beneficial in that a much deeper depth of attack might be required given the limited lateral spreading needed to spall the concrete. Clearly, this assumes that isolated deep pits do not threaten load bearing cross-section and that concrete spalling is more important in bridge applications.

In summary, weathering steels will in principle be of benefit only if wetting and drying occurs in concrete. They will likely have only a slightly better Cl^- threshold than does the carbon steel reinforcement currently used and will likely resist lateral spreading only slightly more than will unalloyed carbon steels. Mill scale is less likely to be important with low alloy and weathering steels than in high Cr steels because there is little Cr to be depleted. These alloys will be inexpensive. However, the improvement in corrosion resistance will likely be small compared to that of carbon steel.

Table 4. Summary of Nominal Compositions (wt. %) of Weathering Steels (ASTM A 588)[50]

Grade	Ni (%)	Cr (%)	Cu (%)	V (%)
A	0.40 max.	0.40-0.65	0.25-0.40	0.02-0.10
B	0.50 max.	0.40-0.70	0.20-0.40	0.01-0.10
Both grades have carbon contents from 0.15%-0.20%; Mn from 0.75%-1.35%; P from 0.04% max.; S of 0.05% max.; and Si from 0.15% to 0.65% with the balance as Fe.				

1% to 5% Chromium Steel Alloys. Martensitic alloys for various applications have been developed over the last few decades. Examples of this type of steel alloy, which in this case is produced by JFE Steel Corporation,[54] are shown in Table 5. Although these steel alloys are produce outside the United States, similar alloys are most likely available from other sources. These alloys are used in power plants and in some oil piping applications.[55] The chloride threshold might be modestly improved because of the low Cr levels and resultant low PREN between 2.5 and 6.4 (see Table 6). The mode of corrosion is likely to be uniform corrosion with oxide-induced spalling of concrete as compared to that of stainless steel with isolated pitting. Because of the unlikelihood of using these alloys as CRR, no further discussion of this alloy family is provided.

Table 5. Summary of Nominal Compositions for 1%-5% Cr Steels (wt.%)[54]

Alloy (Alternative Nomenclature)	C	Mn	P	S	Si	Cr	Mo	V	B (ppm)	Other
Grade 11 (P11/T11/13CrMo 4 4)	0.05-0.15	0.3-0.6	0.025	0.025	0.05-1	1-1.5	0.44-0.65			
Grade 22 (P22/T22/10CrMo 9 10)	0.05-0.15	0.3-0.6	0.025	0.025	0.5	1.9-2.6	0.05-1.13			
Grade 23 (P23/T23/HCM2s)	0.04-0.1	0.1-0.6	0.03	0.01	0.5	1.9-2.6	0.05-0.3	0.2-0.3	5-6	0.03 N, 0.03 Al, 1.45-1.75 W, 0.02-0.08 Nb
Grade 24 (T24/7/CrMoVTiB 10-10)	0.5-0.1	0.3-0.7	0.02	0.01	0.15-0.45	2.2-2.6	0.9-1.1	0.2-0.3	15-70	0.012 N, 0.02 Al, 0.05-0.1 Ti
1CrMoV	0.25	0.8	0.01	0.02	0.2	1	1	0.3		0.004 N, 0.01 Al

Table 6. PREN for Nominal Compositions 1%-5% Cr Steels

Alloy	PREN
Grade 23	2.1-4.1
Grade 22	2.1-6.3
Grade 11	2.5-3.6
1CrMoV	4.4
Grade 24	5.2-6.4
PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 5.	

7% to 12 % Chromium Martensitic Steel Alloys. A recent monograph[56] described the evolution and main uses of 7% to 12% chromium martensitic steel alloys, which are listed in Table 7. In the present study, an additional grouping subdivision was made: nominal 9% Cr (7%-11%) and nominal 12% Cr (11%-12%). The latter group also includes alloys that sometimes are considered stainless steels.

High (7%-12%) chromium originated in the 1910s in Germany,[57] and a short time later in the U.K. The steel developed in Germany by Krupp was intended for steam turbine blades and had 12%Cr:2.5%Mo, whereas Brearley[58] in the U.K. developed a high-temperature steel for gun barrels with a composition of 13%Cr:0.2%C. The (7%-12%) Cr steels were later developed commercially for cutlery knives and tableware, razors, scalpel blades, and heat-resistant tools and bearings.[59]

The 9% and 12% Cr transformable steels with lower carbon (0.1 maximum) contents and small additions of Mo, W, V, Nb, N and other elements have continued to be developed. Applications of these steels encompass petrochemical and chemical plants, gas turbine engineering, oil country tubular goods (OCTG) steel grades, aircraft and aerospace industries, electrical power plants, and nuclear fission reactor components.

The PREN can range from 11 to 20 for this class of alloys, as shown in Table 8. The modern alloys possess higher creep-rupture strength combined with good oxidation and corrosion resistance at high temperatures. Most of the research regarding corrosion behavior has been conducted at high temperatures, because this is the main application of these alloys. From the current literature it is not clear how well these martensitic alloys will behave if embedded in concrete. Some alloys from this family might be worth pursuing further for possible applications as concrete reinforcement. However, research studies on steels subjected to alkaline environments similar to concrete that would allow for the determination of chloride threshold values was not found. Some corrosion performance evaluations in NaCl has been reported,[1] but the temperature was >100^{o}C and subjected to environments with carbon dioxide (CO_2) present at relative high pressure.

7% to 11% Chromium Steel Alloys. Table 7 lists some of the alloys that meet this Cr% composition, and Table 8 provides the corresponding PRENs. One of the currently used CRR, MMFX-2 (ASTM A1035), would be in this category. These alloys are mainly martensitic in microstructure and have PRENs that range, if MMFX-2 is included, from 8.8 to 16.3. If it is evaluated only by the chloride threshold, it is likely that the corresponding values will be smaller than for high Cr steels, as suggested by Tae et al.[23-25] Alloys from this list that show a significant stifling on the oxygen cathodic reduction reaction might warrant being further studied as a possible rebar alternative. In this case, the Cl^- threshold might not be greatly enhanced, but natural propagation rates would be lower. It can be seen in Table 9 that for the various alloys that would fall in the 7% to 11% chromium range, all the PREN values are higher than the value for MMFX-2. Therefore, based on the PREN, each of these alloys has the potential to provide a minimal level of corrosion protection. If a candidate steel were selected from this group, further testing should be performed and include a side-by-side comparison (bracketed with black bar and solid 316 stainless steel) in the laboratory. As in the case of MMFX-2, issues regarding mechanical properties might need to be revisited when investigating these alloys.

Table 7. Summary of Nominal Compositions of 7%-12% Cr Steels (wt.%)

Alloy (Alternative Nomenclature)	Country of Origin	Cr	Ni	Mn	N	C	Mo	V	Si	W	B	Other	Reference No.
E911 (X11CrMoWVNb9-1-1)	Europe	9	0.25	0.51	0.06	0.12	0.94	0.2	0.2	0.9			56
Grade 91 (X10CrMoVNb 91)	Germany	9	0.8	0.45	0.049	0.1	1	0.2	0.4				56
Grade 92 (P92/ T92/ UNS K92460)	U.S.	9		0.45	0.06	0.07	0.5	0.2	0.06	1.8	0.004		56
Grade 9 (P9/T9/ UNS S50400)	U.S.	9		0.45		0.12	1		0.6				56
X18CrMoVNbB91	Germany	9			0.02	0.18	1.5	0.25			0.01		56
SAVE12	Japan	10		0.2	0.05	0.1		0.2	0.25	3		3.0 Co, 0.1 Nb	56
X12CrMoVNbN101	Germany	10			0.05	0.12	1.5	0.2					56
X12CrMoWVNbN1011	Germany	10			0.05	0.12	1	0.2		1			56
TAF	Japan	10.5	0.05		0.1	0.18	1.5	0.2			0.04		56
HCM12A (T122)	Japan	10.0-12.5	<0.5	<0.7	0.04-0.1	0.07-0.14	0.25-0.6	0.15-0.3	<0.5	1.5-2.5	<0.005	0.3-1.7Cu, <0.04Al, 0.04-0.1Nb	56, 60
W.NR 1.4922 (X20CrMoV121)	Germany	10.0-12.5	0.3 - 0.8	<1		0.17-0.23	0.8-1.2	0.25-0.35	<0.5				56
NF12	Japan	11		0.5	0.05	0.08	0.2	0.2	0.2	2.6	0.004	2.5 Cu	56
Duracorr (UNS S41003)	Canada	11.0-12.5	1	1.5	0.03	0.025	0.20-0.30		0.7			0.040 P, 0.015 S	61
W.NR 1.4923 (X22CrMoV12 1) HT91 (SS2317)	Germany Sweden	11.0-12.5	0.3-0.8	0.3-0.8		0.18-0.24	0.8-1.2	0.25-0.35	0.1-0.5				56
HCM12 (JIS SUS410J2TB)	Japan	11.0-13.0		0.4-0.7		<0.14	0.8-1.2	0.2-0.3	<0.5	0.8-1.2		<0.2 Nb	56
EP450	Russia	11.0-13.5	0.05-0.3	0.8		0.1-0.15	1.2-1.8	0.1-0.3	0.5		0.004	0.3-0.6 Nb	56
AL 419	U.S.	11.5	0.5	1	0.1	0.25	0.5	0.4	0.3	2.5			56
AISI 403[a]	U.S./U.K.	11.5-13		0.46-0.53		<0.15			0.2-0.35			0.015 Cu, 0.05 Al	56
AISI 410[a]	U.S./U.K.	11.5-13		<1		<0.15			<1				56
FV607 (12Cr-MoV)	U.K.	11.6	0.62	0.77		0.13	0.89	0.27	0.4				56
M152 (12Cr-NiMoV)	U.S.	11.7	2.65	0.65		0.1	1.6	0.28	0.25				56
CRM12 (12Cr-MoV)	U.K.	11.8	0.96	0.54		0.19		0.3	0.45				56
HT9 (12Cr-MoVW)	Sweden	11.95	0.6	0.6		0.2	1	0.3	0.38	0.52			56
TB12	Sweden	12	0.1	0.2	0.08	0.08	0.5	0.2	0.05	1.8	0.003	0.05 Nb	56
LAPELLOY	U.S.	12	0.3	1		0.3	2.75	0.25	0.25				56
H46	Sweden	12		0.6	0.05	0.15	0.5	0.2	0.4			0.25 Nb	56
Tempaloy F12M	Japan	12					0.7			0.7			56

[a] Table includes some 400 family alloys with nominal 12% Cr.

Table 8. PRENs for 7%-12% Cr Steels

Alloy	PREN
Grade 92	11.1
AISI 403	11.5-13
AISI 410	11.5-13
HCM12A (T122)	11.5-16
NF12	11.8
CRM12	11.8
FI	12.0-13.0
E911 (X11CrMoWVNb9-1-1)	12.1
Duracorr	12.1-14.0
W.NR 1.4922	12.6-16.4
Grade 9	13.3
Grade 91 (X10CrMoVNb 91)	13.3
SAVE12	13.3
X12CrMoWVNbN1011	13.6
W.NR 1.4923, HT91	13.6-16.4
HCM12	13.6-17
X18CrMoVNbB91	14.0
X12CrMoVNbN101	14.1
H46	14.5
FV607	14.5
AL 419	14.7
TB12	14.9
EP450	14.9-19.4
Tempaloy F12M	15.1
HT9	15.3
TAF	16.3
M152	17.0
LAPELLOY	21.1
PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 7.	

Table 9. PREN for 7 to 11% Chromium Steel Alloys

Alloy	PREN
MMFX-2	8.8-10.8
Grade 92 (P92/ T92)	11.1
HCM12A (T122)	11.5-16
NF12	11.8
E911 (X11CrMoWVNb9-1-1)	12.1
W.NR 1.4922	12.6-16.4
Grade 91 (X10CrMoVNb 91)	13.3
Grade 9 (P9/T9/STBA26)	13.3
SAVE12	13.3
X12CrMoWVNbN1011	13.6
X18CrMoVNbB91	14
X12CrMoVNbN101	14.1
TAF	16.3
PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 7.	

Nominal 12% Chromium Steel Alloys. This subcategory is made up of steels with a chromium composition between 11% and 13% Cr, as shown in Table 7. Although some of these alloys could also fall under the category of 12% to 15% chromium steel alloys because of the chromium range, they are discussed here.

As can be seen in Table 10, all of these steels are either martensitic, ferritic, or ferritic-martensitic steel types. The PRENs for the alloys shown in Table 10 range from 11.5 to 21.1.

Table 10. PREN for Nominal 12% Chromium Steel Alloys

Alloy	PREN	Type	Reference No.
AISI 403	11.5-13	Martensitic	37, 56
AISI 410	11.5-13	Martensitic	37, 56
HCM12	11.5-16	Ferritic	62
Duracorr	12.1-14.0	Ferritic-martensitic	63
W.NR 1.4923, HT91	13.6-16.4	Martensitic	56
CRM12	13.6-17	Martensitic	56
FV607	14.5	Martensitic	56
H46	14.5	Martensitic	56
AL 419	14.7	Martensitic	56
TB12	14.9	Martensitic	56
EP450	14.9-19.4	Martensitic	56
Tempaloy F12M	15.1	Martensitic	56
HT9	15.3	Martensitic	56
M152	17	Martensitic	56
Lapelloy	21.1	Martensitic	37, 56
PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 7.			

Of the steels listed Table 10, five are manufactured in the United States and would most likely comply with the Buy America requirements. These steels are:

- AISI 403
- AISI 410
- AL 419
- M152
- Lapelloy

As in the case with the “7% to 11% Chromium Steel Alloys” subcategory, if cost-effective commercially produced rebar can be rolled, a side-by-side comparison of these alloys against carbon steel and 316 stainless steel rebar would be of interest. Again, it would be important to evaluate the mechanical properties of each of these bars in the rolled condition.

12% to 15% Chromium Steel Alloys. Alloys in this section with this range of Cr have been developed for various types of applications. These alloys are listed in Table 11 and have a PREN ranging from 12 to 25 (see Table 12). This section also includes some of the recently developed/modified Cr stainless steels. Moreover, additional modifications of commercially available alloys might be needed to obtain better performance as reinforcing bars.

Some of the most common 12% Cr compositions were introduced earlier. These alloys are being used in boilers and steam turbines. Several programs around the world[55] have produced (and are still developing) new alloys from this family, with the objective of producing efficient low-cost power plants. Hence, the function of these alloys is to increase the maximum operating temperature from the point of view of creep strength and resistance to oxidation in steam. Alloys from this family that are produced in bar form might be considered and tested as possible candidates for a low-cost rebar alternative.

Table 11. Summary of Nominal Compositions of Modified Higher Cr Steels (wt.%)

Alloy (UNS)	Cr	Ni	Mn	N	C	S	P	Mo	Si	Other	Reference No.
(S42200)	11.5-13.5	0.5-1	1		0.2-0.25	0.03	0.04	0.75-1.25	0.75	0.15-0.3V, 0.75-1.25 W	37
(S41426)	11.5-13.5	5.0-6.0	0.05		0.03	0.015	0.02	1.5-2.5	0.5	0.5 V, 0.5 Ti	65
(S41500)	11.5-14.0	3.5-5.5	0.5-2	0.06-0.13	0.05	0.03	0.02	0.5-1	0.6		37
S41425 (SupA)	13.29	4.75	0.73	0.08	0.02	<0.002	0.014	1.6 2	0.27		66
13Cr	12.0-14.0	0.5 max.	0.25-1		0.15-0.22	0.01	0.02		1	0.25 Cu	54
HP13Cr-1	12.0-14.0	3.5-4.5	0.6 max.		0.04 max.	0.01	0.02	0.8-1.5	0.5		54
HP13Cr-2	12.0-14.0	4.5-5.5	0.6 max.		0.04 max.	0.005	0.02	1.8-2.5	0.5		54
420Mod	12.5-14.0				0.18-0.22	0.01	0.02				65
UHP-15Cr-125	14.0-16.0	6.0-7.0	0.6 max.		0.04 max.	0.005	0.02	1.8-2.5	0.5	1.5 Cu	67

Table 12. PREN for Nominal Compositions of Modified Higher Cr Steels

Alloy (UNS)	PREN
13Cr	12.0-14.0
420Mod	12.5-14
(S41500)	14.1-19.4
HP13Cr-1	14.6-18.9
(S42200)	14-17.6
(S41426)	16.5-21.8
HP13Cr-2	17.9-22.2
SupA (S41425)	18-25.5
UHP-15Cr-125	19.9-24.2

UNS = Unified Numbering System; PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 11.

Another subset of alloys in this Cr range is being used in the oil industry: the OCTG alloys. These alloys have been developed to achieve a balance of capital and maintenance costs for use with distributing fluids that are not too corrosive. Base OCTG alloys are 13% Cr steels with a modest amount of C (0.15 to 0.22 wt.%). The modified OCTG alloys reduced the carbon content to ~0.02% and also contain modest amounts of Ni and Mo.[64, 65] These additions are designed to give varying degrees of corrosion resistance according to the chloride concentration, the pressure associated with CO_2 and hydrogen sulfide (H_2S) gases, and temperature. In recent years, modified ferritic stainless steel alloys with low Cr and low Ni (<5 %) + Mo (1%-3%) have been introduced that are similar to alloys that are being developed for OCTG, which are available in only a tubular shape. Two such alloys are UNS S41425 and UNS S41426; their compositions are provided in Table 11. These are likely to be available in a rod/bar shape. Table 11 provides a list of these alloys.

In a recent review, Turnbull and Griffiths[1] highlighted the wealth of data on the laboratory performance of these steels that now exist and that continues to grow. The authors pointed out, however, that "there remains controversy about the relevance of corrosion and environment assisted cracking tests of welded specimens in relation to environmental simulation, surface condition, residual stress, and mechanical test method." Their review,[1] as well as other studies, could be used to assess which of the alloys in Table 11 in the 12%-15% Cr class could be viable candidates for CRR. It is important to note, however, most of these alloys have not been tested in an alkaline solution similar to concrete pore solution.

Ueda et al.[68] found that 13% Cr low carbon steels with Mo $\leq$ 1% showed pitting but did not show pitting when the Mo composition was greater than 2 %. Turnbull and Griffiths[1] indicated that the maximum pit depth should be measured after testing. This is because it is possible that the more resistant alloy could form fewer pits, but each pit may have a greater pit growth rate when compared with alloys that are less corrosion resistant. Felton and Schofield[69] highlighted the general concern about the impact of test time and emphasized the need for staged testing with specimens exposed for varying periods of time.

If available in rod/bar shape, HP1-13Cr, HP2-13Cr, or UHP-15Cr, or the equivalent thereof, could be also considered as a possible rebar alternative.

Low-Nickel Stainless Steels (>15% Chromium). One promising class of materials that could provide a possible low-cost, highly corrosion-resistant bar is the 200 series stainless steels, known as low nickel austenitic stainless steels. These stainless steel alloys were developed in the 1930s. One of their characteristics is that they are also austenitic stainless steels, which might create possible confusion with the 300 class of alloys stabilized by Ni, Mn, and C. The 200 class of alloys have been in use in India since the 1980s and most recently in China (however, the quality control has been inadequate in China, as shown from the results on the alloys tested in references[70, 71]). Although the corrosion resistance of alloys from the 200 series is lower than that for 316 (and even 304) in more corrosive environments, the 200 series might perform adequately as alternative rebar material in concrete.

Almost complete replacement of nickel is possible in the 200 series through the addition of more manganese and carbon as alternative austenite phase stabilizers. This led to the development of grades such as Nitronic 30 (S20400), with Nitronic being a trade name of AK Steel Corporation. The Nitronic grades of stainless steels contained many manganese sulfide inclusions that caused pitting and even stress corrosion cracking.[72] Modern 200 series stainless steels such as 201, 201LN, 202, 204L, 205, 214, and 216 contain from 1% to 7% Ni. The austenite phase is stabilized with Mn, N, and C instead of Ni. One drawback to the addition of Mn as an austenite phase stabilizer is that it lowers Cr solubility, which would be detrimental to corrosion resistance. It can be seen from Table 13 that the Cr contents of many 200 series stainless steels are lower than that of typical 300 series stainless steels, which has ramifications for corrosion in concrete. The claim is that 201LN (UNS S20153) contains nitrogen, which improves corrosion resistance in the presence of Cr, although the mechanism is uncertain. Manganese also increases the solubility of nitrogen in the austenitic phase, which is beneficial. Indeed, the PREN, shown in Table 14, varies from 16 to 28.7; solid 316LN bar has a PREN of 33.3. Caution is warranted in that the PREN calculated in Table 14 does not reflect the effects of variations in S, P, or C. Finally, Talley Metals Technology, Inc., is producing rebar products Enduramet 32 and Enduramet 33, which are listed in Table 13 along with several other alloys from the 200 series.

Table 13. Summary of Nominal Compositions of Lean-Ni Stainless Steels (wt. %)

Type	UNS	Nearest Equivalent	Cr	Ni	Mn	N	C	S	P	Mo	Cu	Si	Reference No.
205	S20500		15.5-17.5	1.5-3.5	14-15.5	0.32 - 0.4	0.12-0.25	0.03M					73
204Cu	S20430		15.5-17.5	1.5-3.5	6.5-9	0.05-0.25	0.15	0.03			2.0-4.0		74
204L	S20400		15-17	1.5-3	7.0-9.0	0.15-0.3	0.03	0.03	0.04		1	1	70
201LN	S20153		16.0-17.5	4.0-5.0	6.4-7.5	0.1-.25	0.03	0.015	0.045	---	1.00	0.75	70, 75
201	S20100	1.4371, 1.4372	16.0-18.0	3.5-5.5	5.5-7.5	0.25	0.15	0.03	0.06			1	73
434	S43400	1.4113 X6CrMo17-1 SUS434	16-18	0.5	1		0.08			.75-1.25		0.6	73
440	S44002		16-18	--	1		0.6-0.75	0.03	0.04	0.75		1	73
HSS1			16.3	0.22	8	0.23	0.06	0.002	0.02		2	0.2	76, 77
HSS2			16.5	1.5	8.5	0.25	0.04	0.001	0.01	2	0.25	0.2	76, 77
EnduraMet 32	S24100		16.5-19	0.5-2.5	11.-14.	0.2 to 0.45	0.15M	0.03M	0.06M		1 M		35
HSS3			16.6	2.3	11.3	0.16	0.03	0.01	0.01	0.12	2.5	0.4	76, 77
214	S21400		17.0-18.5	1.0M	14-16	0.35min	0.12M	0.03M					70
202	S20200	1.4373	17.0-19.0	4.0-6.0	7.5-10.0	0.25	0.15	0.030					73
EnduraMet 33	S24000		17-19	2.5 - 3.75	11.5-14.5	0.2 - 0.4	0.08M	0.03M	0.06M		1 M		36
216	S21600		17.5-22	5.0 - 7.0	7.5-9	0.25 - 0.5	0.08M	0.03M		2.0-3.0			70, 73
444	S44400[a]	1.4521 X2CrMoTi18-2	18.2	0.5	0.3	0.015	0.013	0.002	0.03	1.9			37
AL2003	S32003		19.5-22.5	3.0-4.0	2	0.1-0.2	0.03	0.02	0.03	1.5-2		1	78
	S32001		20	1.6	5	0.13	0.02				0.3	0.4	70

UNS = Unified Numbering System; M =maximum.
Balance of alloy composition is Fe.
[a] In addition, contains 0.27 Columbium and 0.13 Titanium (Ti).

Regarding corrosion performance, views vary somewhat. ATI Alleghany Ludlum[79] claims 201LN demonstrates good corrosion resistance that is comparable to 304L, plus slightly higher strength than 304L. The 304L is claimed to have slightly better pitting and crevice corrosion resistance, but the results are not quantified. They are likely from laboratory tests that provide a relative ranking but provide no insight into the behavior in concrete. Bautista et al.[80] claimed that the corrosion resistance of low-Ni 204Cu reinforcement in $Ca(OH)_2$ + various percentages of NaCl is nearly equivalent to that of 304, 316, 316Ti, and the L grades of these alloys. However, a close inspection of the data reveals lower pitting potentials, higher pit growth rates, and possible widespread pitting compared to the isolated pitting observed by Hurley and Scully[81, 82] in 300 series stainless steels. It also should be noted that open circuit potentials (OCP) for these alloys are similar to that of 300 series stainless steels in $Ca(OH)_2$ + NaCl solutions. Thus, the difference between the OCP and pitting potentials is small. Last, the techniques use by Bautista et al.[80] may be questioned. Potentiodynamic polarization may be an ineffective technique since upon rapid scan it tends to overestimate long-term pitting potentials or not identify them at all if breakdown does not occur before oxygen evolution or transpassivity, as is discussed later. Moreover, polarization-type experiments should be repeated with crevices representing the aggregate present in concrete. Blanco et al.[83] used electrochemical impedance spectroscopy (EIS) to investigate the passive film on 204Cu in carbonated solutions with various amounts of chlorides. It was determined that EIS was not that informative with regard to describing differences between materials pertinent to the Cl^- threshold. However, low uniform

Table 14. Calculated PREN for Lean-Ni Stainless Steels

Alloy	PREN
204Cu	16.3-21.5
EN 1.4372	16.8-22.0
204L	17.4-19.4
S20400	17.4-21.8
S20153	17.6-19.1
EN 1.4373	17.8-23
EN 1.4371	18.4-20.2
S44002	18.5-20.5
S43400	18.5-22.1
HSS3	19.6
S24100	19.7-25.4
HSS1	20
S20100	20.0-22.0
S24000	20.2-25.4
S24000	20.2-26.2
S20500	20.6-23.9
202	22
S32001	22.1
S21400	22.6-24.1
S44400	24.7
AL2003	26.1-30.7
HSS2	27.1
S21600	28.1-39.9
PREN = pitting resistance equivalency number. The PREN values were calculated using the compositions provided in Table 13.	

corrosion rates were obtained, indicative of passive material, and these rates were below the limits normally deemed satisfactory in concrete. Bautista et al.[84] recently assessed the corrosion performance of 204Cu when welded and compared it to that of 304 and 2205 steels. Alloy 204Cu showed a significant reduction in pitting potential after welding.[84] Furthermore, the use of different cleaning methods, either sandblasting or pickling, on the welded 204Cu did not substantially improve the corrosion resistance.[84] However, welded 304 and welded 2205 exhibited improved pitting resistance after pickling or sandblasting the surface.[84]

Garcia-Alonso et al.[76, 77] recently reported the behavior of new stainless steels that based on its composition would fall within the 200's series; their test also included 304 and 316SS for comparison. Tests were conducted in mortar[76] and in concrete.[77] The samples were cast with various chlorides concentrations that ranged from 2% to 5% by weight of cement. In addition, samples with no chlorides were prepared and partially immersed in NaCl after several months in the laboratory environment. From tests in mortar, Garcia-Alonso et al.[76] found that the breakdown potential was as high as that of the 300 series alloys. The alloys were identified as HSS1, HSS2, and HSS3 (compositions are included in Table 13). Alloy HSS2 behaved the best in both mortar and concrete. Polarization scans conducted in concrete after more than a year of monitoring indicated that HSS2 was able to repassivate in the downward scan as suggested by the current decreasing quickly at a critical potential. Garcia-Alonso et al.[77] commented that based on these polarization curves that if the local breakdown of the film occurs, the pits would not grow to a large size and the surface would then be protected by a passivating film. This is debatable as quite negative repassivation potentials were observed. The authors also concluded that the corrosion rate observed in carbon steel bar was at least 10 times larger than in the stainless steel for the various environments tested. In summary, the performance of the low Ni stainless steel was similar to that of the 300 series steels and was far superior to that of carbon steel. It is notable that the difference between the pitting and open circuit potentials was substantial.

Charles[70] was less effusive in the support of the corrosion resistance of 200 series alloys, pointing out the strong effect of Cr on the pitting potentials and depassivation pH in a range of acidic solutions. Hence, the exact Cr content as reported in Table 13 is critical to bar performance. In carbonated environments, low Ni grades with less Cr may suffer from more widespread pit attack compared with high Ni and Cr 300 series stainless steels[80] but do remain passive. Therefore, the low Cr content of the alloys could make them susceptible to both of these phenomena and more fragile in that variations in Cr or the formation of ferrite phases because of weak stabilization could produce large deviations in corrosion resistance from heat to heat. Stress corrosion cracking and intergranular corrosion are also of concern when carbon content is raised and martensite formation is allowed such as by rolling or other deformation processes that induce a martensitic transformation. Last, Charles[70] pointed out that the sulfur content in the 10s of parts per million (ppm) levels has a strong effect on the corrosion rate of these materials. Previous studies indicated that anodic dissolution rates greater than 1 $\mu A/cm^2$ can damage a structure in 10 years.[85]

However, Bautista et al.[80, 84]agreed that further long-term testing in concrete would be required for the low nickel reinforcements. In terms of interpreting these findings as related to initiation, propagation, and oxide spalling, the following comments may be made about the low-nickel stainless steels. The Cl^- threshold for corrosion initiation should be lower than that for 300 series stainless steels such as 316 or 316L, but it might approach that of 304 stainless steel in the optimal metallurgical condition and thus depends critically on the exact alloy. The threshold will, of course, be much better than that of carbon steel. The threshold will likely be very susceptible to changes induced by compositional and microstructural changes. In addition, the lower nickel alloys tested would be very susceptible to problems related to mill scale. As discussed previously, mill scale may result in chromium depletion near the surface. Since these alloys already "flirt" with low Cr contents because of the negative effect of Mn on Cr solubility, the further depletion of Cr could be an issue of concern. Clearly, a descaled alloy would be more desirable with nitric acid passivation to maximize the amount of Cr in the passive film and near surface region. Corrosion could propagate at a fast rate if pits are formed and it is likely these alloys will pit more uniformly. In studies by Torres-Acosta and Sagüés,[45, 46]and later in studies by Hurley and Scully,[7, 10] the ratio of the lateral extent of corrosion and the radial penetration depth were important factors in determining whether spalling by oxide wedging was possible. The low nickel alloys would be expected to be worse than 300 series stainless steels but better than carbon steel from this point of view. Finally, there is no reason to expect that the corrosion product oxide would have a different molar volume than carbon steel, unless the high Mn content exerted an influence here.

Effect of Surface Condition

The effect of rebar surface condition on corrosion initiation can be investigated by testing rebar materials with and without mill scale. It is important to note that stainless steel manufacturers recommend mill-scale removal, but not removing the mill scale remains a tempting way to save costs. The results of the studies discussed here are consistent with manufacturer recommendations for removal of mill scale. The issue originates from the treatment of the rebar after it has been rolled, which determines the surface condition. The bars develop a thick oxide layer (mill or furnace scale) following heat treating during processing. The oxide, which forms at a high temperature, can deplete chromium from the alloy and thus produces an outer metallic layer with a lower corrosion resistance than the parent metal.[86] The passivity afforded by chromium on stainless steel is lost in the outer layers of the rebar alloy. Moreover, formation of a less adherent and possibly anion selective oxide layer exposes a chromium-depleted steel surface.[87] Because of the loss of corrosion resistance by the outer surface layers, most final stainless steel products used in other applications receive a pickling or acid wash to remove the thermal oxide layer and facilitate formation of a stable chromium-containing passive oxide layer to maximize corrosion resistance (ASTM A380). The rebars used in the study by Scully and Hurley,[10] with the exception of solid 316LN stainless steel and 316L Clad, were received with an existing mill scale. The solid 316LN and 316L clad rebar received a pickling treatment prior to being shipped from the manufacturer.

Mechanical Properties

An example of a stress-strain curve for various types of rebar is shown in Figure 1. Clearly, the yield strength for the different types of reinforcement varies. The carbon steel, 2205, Nitronic 32, 316 clad bar, and stainless steel 316LN bars exhibit similar yield stress values, but the yield stress for the MMFX2 is clearly higher. This difference in mechanical behavior could require a change in reinforcement design depending on where the steel is located in the structure and the intended function of the steel. Reinforcement design is outside the scope of this study, but it is important that each new type of CRR be evaluated in an as-received condition to determine the mechanical behavior under uniaxial loading conditions to ensure proper use. Figure 2 illustrates how the amount of cold working can have a significant influence on the yield strength, tensile strength, elongation, and hardness characteristics of steel. All of this helps illustrate why it important to perform mechanical testing in conjunction with the corrosion resistance testing of candidate materials.

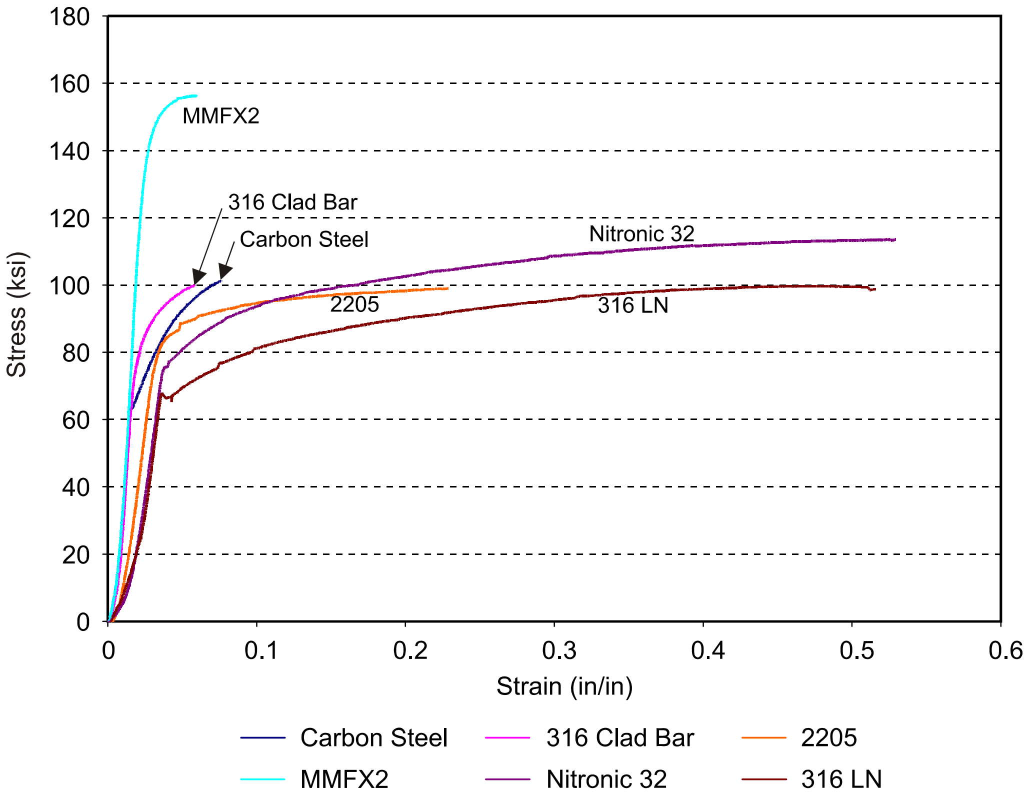

Figure 1. Typical Uniaxial Tensile Test Results for Carbon Steel and CRR Bars

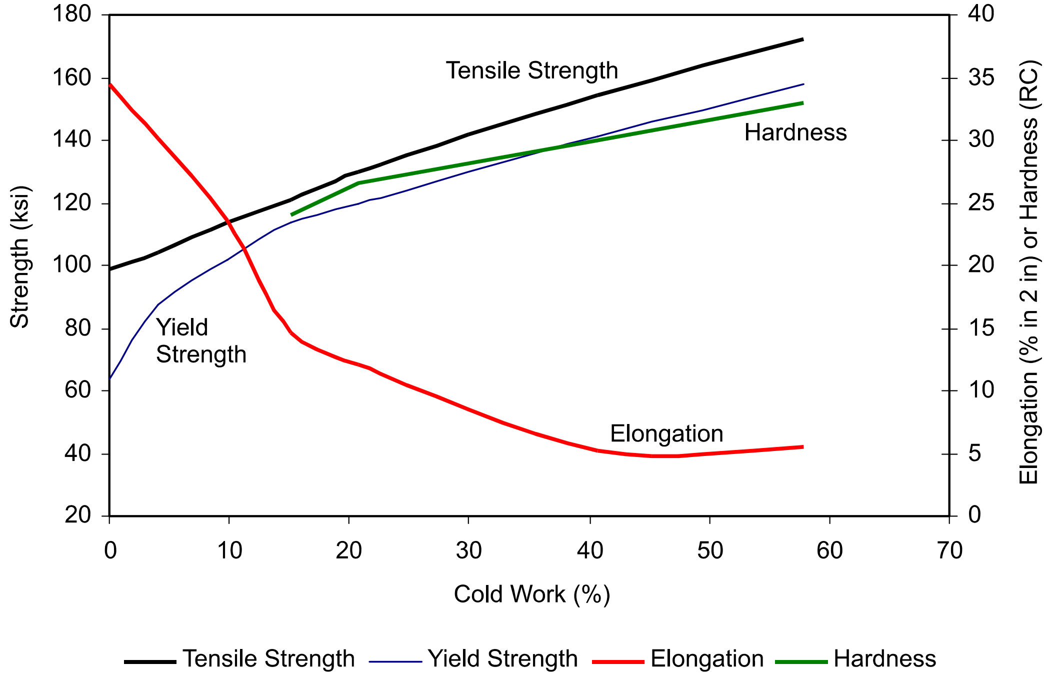

Figure 2. Influence of Cold Work on Strength, Elongation, and Hardness of Duplex Stainless Steel Alloy[88]

Carbon Steel

ASTM A615 comprises the standard specification for carbon steel bars for concrete reinforcement.[29] Three grades are specified: Grade 40, Grade 60, and Grade 75. Table 15 summarizes the minimal mechanical property requirements for carbon steel bars.

Table 15. Required Mechanical Properties for Carbon Steel Rebar (ASTM A615)[29]

Tensile Property		**Grade**		
		40	**60**	**75**
Yield strength, ksi [MPa]		40 [280]	60 [420]	75 [520]
Tensile strength, ksi [MPa]		60 [420]	90 [620]	100 [690]
Elongation, %	Bar Size, No.			
	3	11	9	7
	4, 5	12	9	7
	6	12	9	7
	7,8	---	8	7
	9, 10, 11	---	7	6
	14, 18	---	7	6

It is important to note that ASTM A615 does not prescribe the chemical composition of the steel. Although this specification requires the manufacturer to determine the percentages of carbon, manganese, sulfur, and phosphorus, it only limits the phosphorus content to 0.06%.[29] This is different from the other reinforcing bar standards, which set limits for the chemical composition for each heat.[30, 31, 89, 90] Although ASTM A615 does not designate the steel type, most of the reinforcing steel would be classified as either a low- or medium-carbon steel. Therefore, mechanical properties of the candidate steels will be evaluated based on the tensile properties listed in Table 15, as well as the material characteristics for a low or medium carbon steels as a point of reference. It is again important to note that these properties are not based on steels that have been formed into rebar and that the forming process could substantially alter these properties.

Low Alloy Steels and Weathering Steels

Weathering steels are low alloy steels as described in ASTM A242 and ASTM A588. Their strengths are summarized in Table 16. Regarding mechanical properties, they are comparable to lean-Ni stainless steels but with slightly lower ductility than austenitic stainless steels. The fatigue strength based on ultimate tensile strength should approach 17 ksi. Based on yield strength, tensile strength, and elongation, these steels would most likely exhibit mechanical properties similar to those of a carbon steel rebar.

Table 16. Strength and Ductility of ASTM 588/A and 588M Grade Weathering Steels[50]

Yield Strength, ksi [MPa]	**Tensile Strength, ksi [MPa]**	**Elongation (%)**
50 [345]	70 [485]	18

Alloys with 1% to 5% Chromium

Mechanical properties for alloys discussed previously with 1% to 5% Cr are listed in Table 17. The yield strength of these materials can be as low as 30 ksi or as high as 84 ksi, with an ultimate tensile strength range of 60 to 100 ksi. This tensile strength translates into a fatigue strength of approximately 15 ksi. Based on yield strength, tensile strength, and elongation, these steels would most likely exhibit mechanical properties similar to those of a carbon steel rebar.

Table 17. Mechanical Properties of Steel alloys with 1-5% Cr Steels [54]

Alloy	**Yield Strength, ksi [MPa]**	**Tensile Strength, ksi [MPa]**	**Elongation (%)**
Grade 11	29.7 [205]	60.1 [415]	30
Grade 22	29.7 [205]	60.1 [415]	30
Grade 23	58.0 [400]	73.9 [510]	20
Grade 24	84.1 [580]	97.1 [670]	20

High-Chromium Martensitic Steels (7%-12% Chromium)

Mechanical properties for alloys discussed previously with 7% to 12% Cr are listed in Table 18. The yield strength of these materials can be as low as 30 ksi and as high as 70 ksi. The ultimate tensile strength ranges from 60 to nearly 100 ksi. This tensile strength translates into a fatigue strength of approximately 15 ksi as in the case of other iron-chromium alloys. Based on yield strength, tensile strength, and elongation, these steels would most likely also exhibit mechanical properties similar to those of a carbon steel rebar.

Table 18. Room Temperature Mechanical Properties of 9%-12% Cr Martensitic Steels[56]

Alloy	Yield Strength, ksi [MPa]	Tensile Strength, ksi [MPa]	Elongation (%)
Alloy 122	58 [400]	89.9 [620]	20
Grade 9	29.7 [205]	60.2 [415]	30
Grade 91	60.2 [415]	84.8 [585]	20
Grade 92	63.8 [440]	89.9 [620]	20
Tempaloy F12M	68.1 [470]	99.3 [685]	18
X20CrMoV121	71.8 [495]	98.6 [680]	16

Alloys with 12%-15% Chromium (Nominally Alloys with 12% and 13% Chromium)

Table 19 shows the mechanical properties of these alloys, which indicate slightly greater strengths in the 80 to 110 ksi yield strength range and tensile strengths between 95 and 140 ksi. Based on yield strength and tensile strength, these steels would most likely exhibit mechanical properties greater than those for carbon steel rebar.

Table 19. Summary of Mechanical Properties of Modified 13% Cr Steels

Alloy	Yield Strength ksi [MPa]	Ultimate Tensile Strength (min) ksi [MPa]	Elongation (%)	Reference No.
13CR-80	80-95 [551.7 – 655.2]	95 [655.2]		91
13CR-95	95-110 [655.2 – 758.6]	105 [724.1]		91
HP1-13Cr-95	95-110 [655.2 – 758.6]	105 [724.1]		91
UHP-15Cr-125	125-150 [862.1-1034.4]	135 [931]		91
S41425	95 [862.1]	132 [907]	29.5	66
S41500	90 [620.7]	115 [793.1]	15	37
420 Mod	80 [551.7]	100 [689.6]		65
Lapelloy-S42300	110 [760]	140 [965]	8	37

200 Series of Low-Nickel Stainless Steels (>15% Chromium)

A summary of the mechanical properties of lean-Ni stainless steels is provided in Table 20. Enduramet 32 and 33 and the 200 family of alloys contain Cr >~ 15%. Allegheny Ludlum [79]claims that the strength of AL201LN is superior to that of 304L and equal to that of Nitronic 30 but with better elongation. The superior strength is attributed to N and C in solid solution. The elongation is better. When nitrogen and carbon contents are reduced, the alloys can be prone to martensite formation and may become more brittle because of cold cracking and susceptible to stress corrosion cracking.[70] Low wt.% Ni alloys are not only more prone to cold cracking and experience a ductile to brittle transition but may be more susceptible to corrosion than is 300 series stainless steel. The yield strength of these materials range from 45 to 78 ksi; the tensile strength ranges from 70 to 111 ksi with an elongation greater than 25%. Given this tensile strength, a fatigue strength of 17 to 28 ksi might be expected. These alloys likely possess a fracture toughness 100 MPa $(m)^{1/2}$ excluding any cold cracking effects, although specific information was not obtained. In general, based on yield strength, tensile strength, and elongation, these steels would most likely exhibit mechanical properties similar to those of a carbon steel rebar.

Table 20. Summary of Typical Mechanical Properties of Lean-Ni Stainless Steels

Alloy (UNS)	Yield Strength, ksi [MPa]	Tensile Strength, ksi [MPa]	Elongation, (%)	Reduction in Area, %	Hardness, HRB[a]	Reference No.
201 (S20100)	40 [275]	75 [515]	40	45	100 max.	37, 73
202 (S20200)	40 [275]	75 [515]	40	45	---	37, 73
201LN (S20153)	45 [310.3]	95 [655.2]	45	---	---	75
Nitronic 30 (S20400)	48 [331]	95 [655]	35 min	---	100 max.	92
204Cu (S20430)	47 [324]	96 [662]	62	80	90	74
205 (S20500)	65 [450]	115 [790]	40	---	100 max.	37, 73
216 (S21600)	50 [345]	90 [620]	40	---	100 max.	37, 73
Enduramet 32 (S24100)	55 [380] 84 [579.3][b]	100 [690] 121 [834.5][b]	30 42[b]	50		35
Enduramet 33 (S24000)	55 [380] 75 [517.2][b]	100 [690]	30	50	100 max.	36, 92
Nitronic 19D (S32001)	69-78 [476-537.931]	100-111 [689.7-765.5]	31-40			88
AL2003 (S32003)	65 [450]	95 [655]	25		31 HRC	78
434 (S43400)	53 [365]	77 [530]	23		83 max.	37, 73
444 (S44400)	40 [275]	60 [415]	20		95 max.	37, 73

UNS = Unified Numbering System; HRB = Hardness Rockwell B, HRC = Hardness Rockwell C.
[a] Plate/sheet/strip product form.
[b] Hot-rolled unannealed condition.

Cost Considerations

Unlike traditional reinforcement, CRR can be more sensitive to the cost of the alloying elements. The sensitivity of the CRR to cost fluctuations will depend on two factors: the cost of the individual alloying element and the quantity required for a given steel alloy. Figure 3 shows the influence of three alloying elements on the average surcharge rate for 200 and 300 series austenitic stainless steels from January 2001 to May 2008.

In Figure 3, it is clear that austenitic stainless steels are sensitive to nickel pricing, with the 200 series exhibiting less of a change when compared to the 300 series. Both series strongly reflect the increase in nickel pricing over the last 7 years. The increase in cost for molybdenum also increases the cost for certain austenitic stainless steel alloys. However, not all of the austenitic stainless steels include molybdenum, and therefore the strong increase in molybdenum pricing that is shown in Figure 3 is not strongly reflected in the 200 and 300 series surcharge rates. Finally, relative to the cost of nickel and molybdenum, the cost of chromium has only slightly increased. Although stainless steels require relatively higher chromium contents when compared to ordinary steels, it is clear that this element has little effect on the surcharge rate. Therefore, steels with lower nickel and molybdenum should be selected to ensure lower surcharge rates; elevated chromium compositions should not be of concern.

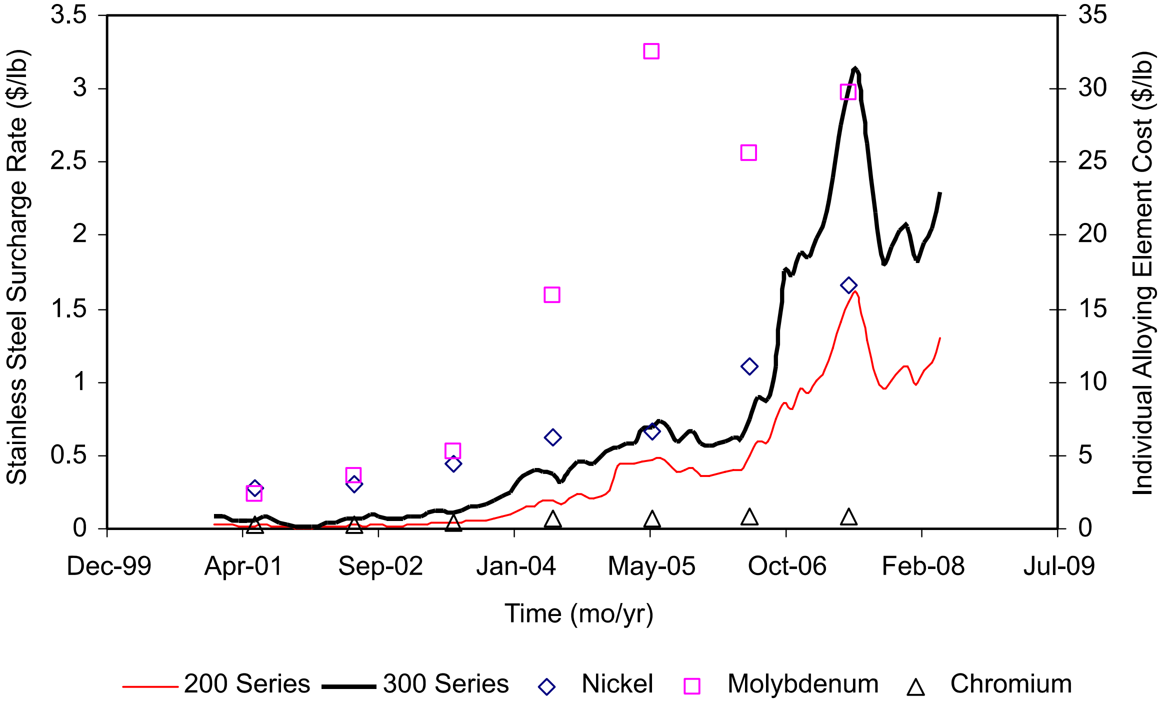

Figure 3. Influence of Alloy Cost on Average Surcharge Rate for Austenitic Stainless Steels

Different types of stainless steels require certain alloys in sufficient quantities to promote the formation of desired microstructures. Iron and carbon are not included in the following discussion as required components because they are key ingredients in all steels. Austenitic stainless steels contain alloying elements that favor the formation of austenite (face-center cubic crystal structure), such as manganese, nickel, or nitrogen.[37, 73] Ferritic stainless steels are chromium alloys that form a body-center cubic crystal structure.[37, 73] Martensitic stainless steels are chromium alloys that generally have a higher carbon content than the ferritic stainless steel and form a body-center tetragonal crystal structure.[37, 73] Duplex stainless steels are chromium-nickel alloys that contain two phases (ferrite and austenite) and can also include alloying elements such as copper, molybdenum, nitrogen, or tungsten.[37, 73] Precipitation-hardening (PH) stainless steels are chromium-nickel alloys with aluminum, copper, niobium, or titanium added to enhance desired features and differs from the other four types in the manner of heat-treatment used.[37, 73] The differences in these steels not only affects the physical characteristics of the steel, but can also strongly influence the cost of producing a certain type of steel. In Figure 4, the average surcharge for the ferritic and martensitic stainless steels remains much lower when compared to that of the other types of stainless steel. It is also apparent that austenitic, duplex, and PH stainless steels are influenced by the cost of nickel, which is expected upon evaluation of the composition of each of these steels. Therefore, over the last 7 years, the ferritic and martensitic stainless steels have demonstrated the smallest change as alloying cost changed.

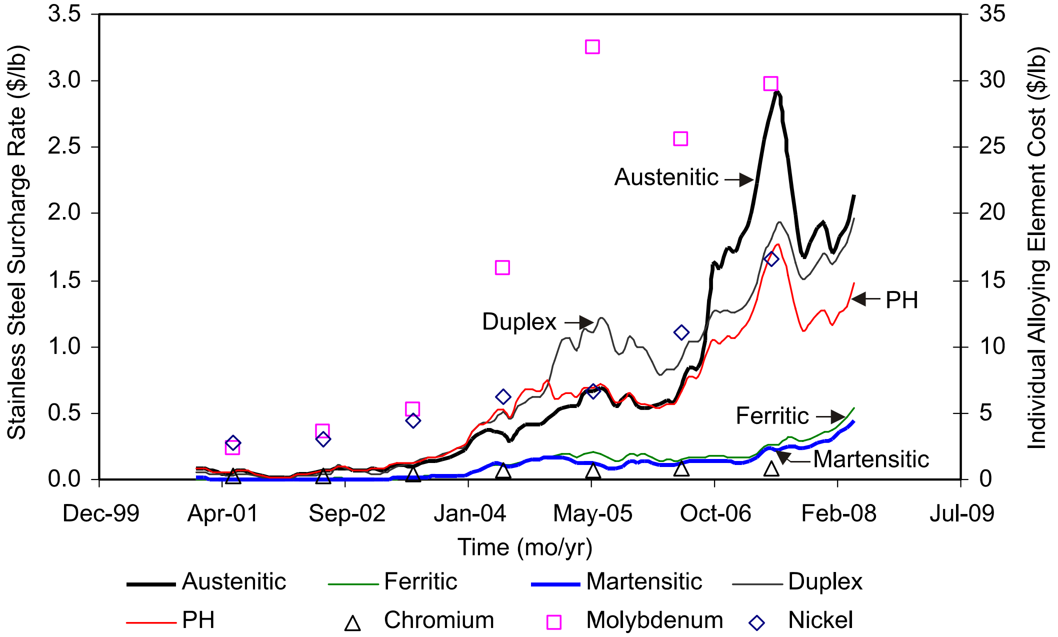

Figure 4. Effect of Nickel, Molybdenum, and Chromium Pricing on Surcharge Rate for Different Types of Stainless Steel

Finally, some of the products in this report include plate, bar cut from plate, shapes cut from plate, pipe through various suppliers, and pressure vessel heads. The cutting of bar from plate might raise prices, which may partially offset the low cost compared to high-Ni stainless steels.

Recommended Corrosion Test Methods for Evaluating CRR

A list of recommended tests to asses the viability of the suggested new materials for reinforcing steel was compiled. The corrosion tests identified evaluate behavior during both the initiation and propagation stages. Tests that could be conducted to rank the identified low-cost CRR materials are divided between laboratory electrochemical tests and field tests. In field tests, performance during exposure to concrete is assessed (which would include concrete test slabs); laboratory tests typically focus on simulated pore solutions and the use of electrochemical methods. The electrochemical methods used in the laboratory include open circuit potential (OCP), polarization resistance (R_p), and potentiostatic measurement of the chloride threshold.

Tests that indirectly address corrosion propagation within concrete might include determination of bond strength of reinforcing bars embedded in concrete and studies of concrete cracking induced by corrosion products (because of pressure created by corrosion product formation). To evaluate resistance to initiation, accelerated corrosion tests, such as ASTM G109[93] or the Florida Department of Transportation (FDOT) tombstones method,[21] and mechanistic electrochemical tests (anodic site spreading and galvanic couple experiments) in simulated pore solutions at various levels of chlorides may be considered.

Laboratory Electrochemical Tests

Test Method for Chloride Threshold Determination

The chloride threshold value for carbon steel is independent of the method used to obtain it. Techniques to determine the chloride-induced threshold level for active corrosion on rebar include corrosion rate determination via linear polarization resistance (LPR), macrocell current measurement,[93] OCP monitoring, potentiodynamic critical potential determination, and potentiostatic testing for anodic current rise. Chloride threshold results for carbon steel from potentiodynamic tests (Cl^-/OH^- ratio of 0.6) and incremental chloride addition potentiostatic experiments (Cl^-/OH^- ratio between 0.25 and 0.34) were consistent with previously published results using other methods ($0.25 < Cl^-/OH^- < 0.8$).[94-98] A chloride threshold Cl^-/OH^- ratio of 3.7 was found for MMFX-2, approximately 6.2 times the chloride threshold of carbon steel, which is in agreement with testing conducted in concrete.[99]

However, potentiodynamic scans are sometimes ineffective for determining potentials associated with chloride-induced breakdown of passivity on more corrosion-resistant materials such as 316LN and 2101 duplex stainless steels in the $Ca(OH)_2$ environment. One interpretation is that the incubation time for passivity breakdown via chloride penetration into the passive film is not satisfied in the case of fast potentiodynamic scans prior to attainment of high potentials during upward scans. Oxygen evolution can occur on highly corrosion-resistant stainless steels prior to breakdown and pitting during upward potentiodynamic scans at all chloride concentrations tested. Potentiostatic techniques were found to be effective methods for characterizing the chloride thresholds of corrosion-resistant rebar materials because (1) the incubation time could be satisfied and (2) breakdown of passivity was easily detected by a current rise even if one small site was responsible. The chloride threshold obtained from potentiostatic tests represents the condition when the applied potential (such as study +200 mV vs. saturated calomel electrode [SCE]) exceeds a chloride-dependent threshold potential for chloride-induced corrosion. Previously published chloride thresholds for carbon steel obtained from potentiostatic tests show little effect of applied potential when conducted above -200 mV vs. SCE.[99, 100] However, the critical potential for chloride-induced pitting or depassivation is known to be dependent on chloride concentration for stainless steels in sulfuric acid solutions.[72] Previous results also indicated a potential dependency of 316LN in saturated $Ca(OH)_2$ for stainless steels.[17] It is important to note that a chloride threshold could not be determined for 316LN stainless steel during testing conducted at 0 and -0.2 V vs. SCE in saturated $Ca(OH)_2$ because of NaCl saturation of the solution prior to corrosion initiation.[17]

Unfortunately, conventional methods for determining the corrosion rate and subsequently the chloride threshold for carbon steel rebar, such as LPR and macrocell current monitoring,[101] may not be effective for highly alloyed bars because of the difference in the morphology of chloride-induced corrosive attack. Stainless steels suffer from highly local pitting and remain passive over large areas of the surface while carbon steel undergoes global depassivation and corrosion of large areas ultimately occurs. It has been shown that LPR is limited in its ability to detect localized corrosion when isolated corrosion occurs because the active area emitting a high current (or possessing a small polarization resistance) is a small fraction of the total area.[102] Moreover, methods for detecting the presence of localized corrosion through polarization resistance measurements are highly dependent on the experimental procedures and parameters chosen for analysis.[102, 103] Mansfeld et al. noted the presence of pits through visual and microscopic observation that went undetected by the accompanying impedance spectra.[103] This situation exists when a small fraction of the surface area undergoes pitting and the remainder of the surface remains passive, but the exact conditions for detection depend on the polarization resistance of the active and passive areas, the area fractions, and the test frequency or scan rate. Similar arguments apply to the macrocell method. Macrocell current measurements, such as ASTM G109, could also in theory provide diminished ability to detect localized corrosion. Detection of corrosion relies on galvanic current flow between a top and bottom rebar in a concrete block. Widespread depassivation and anodic dissolution on a carbon steel anode are likely supported by large cathodic reactions on the rebar in the bottom mat. However, if the top rebar in a concrete block develops small pit sites, then the remainder of the top rebar may serve as a local cathode and little galvanic current may be measured with respect to the bottom rebar. The resulting macrocell current would indicate passivity, despite the possible presence of localized attack. When large anodes are quickly developed on the top bar, the galvanic current to the bottom (chloride-free bar) is larger and may be detected as soon as corrosion is initiated. The latter is the conventional case with carbon steel rebar. It should be noted that results of studies by Clemeña and Virmani from testing conducted in chloride-contaminated concrete of 316L defective clad bars demonstrated that macrocell current monitoring may detect corrosion of the carbon steel core provided that the defect size is adequately large.[11] However, LPR and macrocell measurements may not be reliable techniques to measure meaningful corrosion rates or chloride thresholds for corrosion initiation of highly alloyed stainless steels if the percentage of the activated corrosion area is small. Although LPR is an effective tool for carbon steel, where a drop in polarization resistance signals chloride-induced activation over large surface areas, it seems at best a very insensitive test for detection of chloride-induced corrosion on alloyed rebar materials when large areas remain passive with a high polarization resistance.

The potentiostatic method offers a technique to probe and detect the onset of a high corrosion rate at the weakest link present, regardless of size. There is likely no critical active corrosion defect size that may escape detection since small increases in current attributable to the breakdown of passivity are detectable. It is important to note that in potentiostatic mode, cathodic current is supplied from the counter electrode (CE) to support anodic reactions at the CE. In galvanic coupling, the corresponding cathodic current is supplied from a combination of the corrosion site itself, the rebar adjacent to the corrosion site, and any other rebar electrically connected. For instance, results from 316L clad rebar from this investigation have shown that any exposure of the underlying carbon steel reduces the chloride threshold to near that of carbon steel. Therefore, the experimental method used to determine the true initiation threshold of chloride-induced corrosion of alloyed and clad rebar materials must enable adequate detection of localized corrosion. Hence, the chloride threshold found from the potentiostatic method using $Ca(OH)_2$ solution is often more conservative than that found using the ASTM G109 method for the same materials.[11, 12] Several explanations may shed light on this difference. First, the presence of $Ca(OH)_2$ crystals in the concrete pore solution of actual concrete may provide extra buffering capacity that resists acidification, as mentioned previously. However, it is difficult to argue that the large reservoir of the saturated $Ca(OH)_2$ solution does not provide more buffering capability than concrete. Second, the OCP of the steel in concrete has not reached +200 mV. Hence, the potentiostatic hold is more severe. Third, the ASTM G109 method may provide information on the chloride threshold concentration for initiation and some necessary degree of propagation (before corrosion is detected) whereas the laboratory test detects the chloride threshold for actual initiation with very little propagation. Fourth, the concrete has a higher ionic resistivity than the saturated $Ca(OH)_2$ solution and may have a greater pH than 12.6.[104] The former is likely more important in the propagation stage whereas the later may effectively lower the Cl^-/OH^- ratio at a given Cl^- concentration.

Test Method for Propagation

The critical issue is whether extremely local active corrosion can damage concrete. In this regard, corrosion at small defects may or may not damage concrete. Accumulation of corrosion products of sufficient volume over a large area of bar is required to create stresses at the concrete/rebar interface that leads to concrete cracking.[53] Therefore, it must be recognized that small pits or small holes in a bar, while actively corroding when the chloride threshold is exceeded, may not lead to concrete damage as readily as global depassivation, as in the case of carbon steel. Both the extent of lateral and radial propagation and the nature of the corrosion products formed must be considered. Electrochemical propagation tests include the artificial pit growth technique with either an infinite cathode or under potentiostatic control, and electrode array spreading type corrosion tests. The galvanic experiment is in use at the University of Virginia[7, 16]and is similar to the University of Kansas test [105] that was funded by Kansas DOT discussed later except that corrosion is usually initiated under potentiostatic control and switched to a galvanic couple during the propagation stage.

Further investigation is required to determine how propagation of localized corrosion sites on alloyed rebar materials will damage concrete structures. From this perspective, one argument is that the ASTM G109 macro-cell method detects the chloride threshold concentration for initiation and some necessary degree of propagation. The reason for this rationalization is that the corroding bar would draw current from the other bars in the concrete block when the anode on the first bar becomes large or when propagation has occurred to a sufficient extent. In this sense, it may provide a parameter that is closer to a chloride threshold for damage, not just initiation. However, such a correlation, although more valuable to engineers, appears fortuitous at this time.

Test Methods for Concrete or Mortar Slabs

In recent years, many sample geometries to test corrosion resistance have been introduced in the literature. The authors recommend two types of tests: (1) a test using macrocell specimens that naturally corrode with a relatively large surface area and (2) a test using specimens where the rebar is subject to potential hold using an external potentiostat.

Another accelerated method is a macrocell test introduced by the University of Kansas as part of a Kansas DOT research project.[105] This uses two containers connected electrolytically via a salt bridge and electronically via a 10-ohm resistor. The solution in the anode side is simulated pore solution with sodium chlorides, whereas the cathode side is filled with simulated pore solution only (no chlorides). Recent reports [105] detail the cell preparation. The rebars could be tested with and without a mortar coating. These accelerated macrocell tests could be as short as 10 months long, although this will depend on the alloy corrosion resistance, how fast the chlorides are introduced, and the thickness of the mortar.

The FDOT tombstone[21] sample geometry began to be used recently by VTRC.[106] This is an interesting geometry to consider. The samples are partially immersed in the solution of interest. Two rebars are partially immersed with the third ending above the water line and serving as a cathode. The potential and current are monitored and activation is detected when a potential drop occurs accompanied with a large current. This onset of corrosion (initiation) and propagation can be monitored.

Hartt et al.[21] has been conducting experiments on samples such as those shown in Appendix B, Figure B.1. The larger exposed area to NaCl ponding than used in the traditional ASTM G109 method makes this specimen attractive. The samples could be placed inside the laboratory or outside and exposed to cyclic weather variations. Cyclic testing would enable investigation of weathering steels said to benefit from wetting and drying. Some of the samples could be prepared with an initial artificial crack that would shorten the exposure time. A detailed description of this sample and method is included in Appendix B. This method consists of longer term exposure to cyclic ponding of reinforced concrete slabs, similar to those currently being investigated at Florida Atlantic University (sponsored by the Federal Highway Administration and FDOT)[21] that involves other alternate rebar materials (black bar, MMFX-2, 3Cr12, 2201, 2304, 304, and 316). Appendix B briefly describes the cell setup. Results to date indicate that the mean time to corrosion initiation for black bar is about 80 days and for MMXF-2 and 2201 about 300 days. These exposures could initially last for 18 months (or more if reinforcing steel is not corroding) but could be subsequently extended if the results so warrant.

The traditional ASTM G109 sample geometry and method could also be considered. A variation on this test was used by Clemeña previously.[11] Despite concerns over the inability to detect a macro-cell current when the anode is small, the results of Clemeña and colleagues[11, 12, 14] were in reasonable agreement with those of Scully and Hurley[10] regarding different candidate CRR materials.

Mortar or concrete samples with a relatively small concrete cover could be polarized to a somewhat noble potential (0, +100 mV vs. SCE, for example). The exposed area could be either ponded (only a portion of the specimen subject to a high-chloride solution) or immersed. The cover, if made of mortar, should probably be no less than 0.39 in (10 mm) thick.[107] A relatively low amount of cement and a high water-cement ratio would shorten the time needed for the chlorides to be transported to the surface of the rebar. In many of these tests, the Cl^- level must be determined by post-test core drilling to sample for Cl^- concentrations.

For marine environments, rectangular concrete/mortar-reinforced prisms simulating partially submerged piles (rebars in the long direction) could be polarized by rebar immersed in a second tank (representing the immersed reinforcement). The concrete/mortar cover thickness should be at least 0.39 in (10 mm); a thickness of 0.79 in (2 cm) is probably better.[107]

Finally, concerning mechanical property evaluation, tests to evaluate cover adhesion, impact resistance, harsh atmospheric condition resistance, and coefficient of thermal expansion tests might prove beneficial.

SUMMARY

Promising CRR Materials

A list of the promising alternate reinforcing bar candidates is provided in Table 21. The most promising alternate reinforcing materials seen to date that are less expensive than 300 series stainless steels are low-Ni austenitic stainless steels, such as 201LN, and a variety of ferritic or martensitic 12% to 15% Cr steels. Low-Ni austenitic stainless steels will likely have inferior corrosion resistance compared to traditional 300 series stainless steels but may constitute a significant improvement over that of traditional ECR. Low-Ni 200 grade stainless steels should be investigated for further elucidation of their properties in both field and laboratory testing. Bar materials identified for further investigation include HSS2, 201LN, Enduramet 32, and Enduramet 33. In addition, 200 series stainless steel containing 1% to 2% molybdenum, such as 216, appear promising if available in bar form. Based on prior results with regard to MMFX-2 (9.3% Cr) steels, which show marginal gains in corrosion performance when compared to carbon steel, but at a very low cost, it is recommended that a 12%-15% Cr steel be selected when increased corrosion performance is needed. In the 13% Cr ferritic or martensitic steel alloy category, S41425, S41426, Lapealloy, and S42300 are recommended. All of these alloys contain 1.5% Mo. Duracorr should also be considered because the PREN and chromium contents are higher than for MMFX-2 and the manufacturer is interested in providing reinforcement steel samples.[106] This is important because corrosion resistance and mechanical properties could be determined for this potentially low-cost steel. Additional research may be required to find a 12%-15% Cr steel that has the optimal product form, PREN, strength, ductility, and cost. If available in rod/bar shape, HP1-13Cr, HP2-13Cr, or UHP-15Cr, or the equivalent thereof, could be also considered as a possible rebar alternative. Steels with 9% to 12% Cr are recommended when the modest improvements in corrosion resistance when compared to carbon steel can be justified by the lower cost . Steels with lower chromium compositions than those previously mentioned likely offer marginal gains in corrosion performance when compared to carbon steel.

Information regarding the material properties of these materials is limited at best. Although data will need to be gathered on specimens that have been rolled to the final reinforcing steel dimensions, some of the bars identified could potentially function in the same capacity as the MMFX-2 that is currently used by VDOT. However, for critical areas that require the bar to yield in a ductile fashion prior to the concrete failing in compression, additional research is required in this area.

Based on cost considerations, nickel and molybdenum can significantly influence the surcharge rate whereas chromium has little influence. Therefore, the most desirable CRR will have a sufficient quantity of chromium and low nickel and molybdenum concentrations. This will reduce the chance of unexpected cost increases because of increases in surcharge rates. It should also be noted that martensitic and ferritic stainless steel alloys on average showed less sensitivity to changes in raw material prices over the last 7 years.

Table 21. Promising Alternate Reinforcing Bar Candidates and Motivation for Investigation

Alloy	Motivation
216	Highest PREN in lean-nickel class, possible synergistic benefit of Cr and Mo
201LN	Commercially available 2XX series alloy with favorable combination of corrosion resistance, mechanical properties, and cost.
4xx/Nitronic 50/ASTM 615	Comparison bars to help rank test materials
Duracorr	Potentially available as rebar. Higher PREN and chromium content than MMFX-2.
Enduramet 32	Talley Metals[a] already producing as bars, and is similar to 201
Enduramet 33	Talley Metals[b] already producing as bars, and is similar to 201
HSS2	High PREN owing to addition of 2% molybdenum
Lapealloy	Available in bar/rod. Combination of Cr + Mo and low Ni content produces a high PREN, approaching 20, with low cost and possible gain in mechanical strength
S41425	Available in bar/rod. Combination of Cr + Mo and low Ni content produces a high PREN, approaching 20, with low cost and possible gain in mechanical strength
S41426	Available in bar/rod. Combination of Cr + Mo and low Ni content produces a high PREN, approaching 20 with low cost and possible gain in mechanical strength
S414300	Available in bar/rod. Combination of Cr + Mo and low Ni content produces a high PREN, approaching 20, with low cost and possible gain in mechanical strength

PREN = pitting resistance equivalency number.
[a] Reference 35.
[b] Reference 36.

Promising Test Methods for Evaluating CRR

The most promising test methods found in this study are summarized in Table 22. The most promising test for determining chloride threshold (initiation) in the laboratory is the +100 mV vs. SCE potentiostatic hold test. The Cl^- threshold can be established for the new rebar materials by conducting potentiostatic hold tests at +100 mV vs. SCE at various fixed Cl^- levels using a method discussed by Hurley and Scully.[81, 82] This test can be conducted with or without crevices.

The +100 mV vs. SCE potentiostatic hold test can also be extended to mortar-covered bars immersed in a simulated pore water solution with a thin mortar layer. In this hybrid laboratory/field test, Cl^- can be added to the mortar mix or to the pore solution.

Propagation tests can also be conducted by either conducting potentiostatic hold tests at selected potentials or galvanic coupling in a split cell. This method was used by Hurley and Scully[71, 72] and is similar to the University of Kansas method.[81, 82, 105] A propagation law and repassivation potential (no propagation threshold) can be established as discussed by Hurley and Scully.[81]

Table 22. Promising Test Methods for Alternate Rebar Studies

Corrosion Property	Test Method	Motivation
Laboratory/initiation	+100 mV vs. SCE potentiostatic test in simulated pore solution, or variation with concrete mortar layer or concrete block[a]	Conservative yet compares well to field/concrete test blocks, reasonable test time, precise determination of threshold Cl^- level, ability to compare to existing research data
Laboratory/propagation	Split cell method of University of Virginia[b] or University of Kansas[c]	Previous use, quantitative determination of propagation rates, ability to construct propagation law
Field/initiation and propagation	ASTM G109[d] or Florida Atlantic University and Florida Department of Transportation tombstone[e]	Ability to compare to existing research data, provides information on practical initiation conditions, ability to apply alternate wetting and drying, can provide information on propagation if continued until concrete spalling results

[a] References 81 and 82.
[b] References 7 and 16.
[c] Reference 105.
[d] Reference 93.
[e] Reference 21.

Concerning field testing, the ASTM G109 method is recommended primarily for comparison to existing research data. In this test, ponding of a Cl^- containing solution on concrete blocks should be attempted. The test can be used to assess Cl^- thresholds either by varying concrete levels in the mortar mix or performing core drilling/sampling. The initial recording of galvanic current indicates initiation, and spalling provides an engineering indication of propagation. The FDOT tombstone method should also be considered as a variation of the ASTM G109 method in a high water/low water (e.g., highly permeable concrete mix) in order to test candidate rebar in concrete at various Cl^- levels.[21] Finally, concrete specimens conforming to the requirements of ASTM G109 and the FDOT tombstone method can be artificially cracked to accelerate the time to corrosion and evaluate a "worst case" bridge deck condition.[108]

To aid in bracketing the unknown candidate materials responses during corrosion testing, comparisons should be made to ASTM A615M carbon steel, MMFX2, 400 series ferritic stainless steels, manganese stabilized austenitic stainless steel (such as a nitronic alloy which are likely to contain a high manganese sulfide inclusion content), and selected 300 series stainless steels (such as 304 and 316LN stainless steels).

Finally, the mechanical properties for each steel will need to be determined. Data will need to be gathered on specimens that have been rolled to the final reinforcing steel dimensions, although some of the bars identified could potentially function in the same capacity as the MMFX-2. However, additional research is required for the higher strength steels for structurally critical areas.

CONCLUSIONS

- Promising alloy candidates for CRR materials are 201LN, HSS2, Enduramet 32, Endurament 33, 4xx/Nitronic 50/ASTM 615, 216, Lapealloy, S41425, S41426, S414300, and Duracorr.
- A promising laboratory test method to evaluate corrosion initiation is the +100 mV vs. SCE potentiostatic test in simulated pore solution[81, 82]or a variation of this test with concrete mortar layer or concrete block.[21]
- A promising laboratory test method to evaluate corrosion propagation is the split cell method of the University of Virginia[7, 16]or the University of Kansas,[105] which was funded by the Kansas Department of Transportation.
- Promising field test methods to evaluate corrosion initiation and propagation are ASTM G109 and the Florida Atlantic University and Florida Department of Transportation tombstone method,[21] both of which can be performed on cracked and uncracked specimens.[106-108]

RECOMMENDATIONS

1. *VTRC should work with VDOT's Materials Division to establish a procedure for evaluating future CRR candidates.*
2. *VTRC should evaluate the corrosion resistance of 201LN, HSS2, Enduramet 32, Endurament 33, 4xx/Nitronic 50/ASTM 615, 216, S41425, S41426, S414300, Lapealloy, and Duracorr to identify alternative candidate reinforcing steel bars for VDOT bridge decks.*
3. *VTRC should evaluate the mechanical, developmental length, and physical properties of 201LN, HSS2, Enduramet 32, Endurament 33, 4xx/Nitronic 50/ASTM 615, 216, S41425, S41426, S414300, Lapealloy, and Duracorr to identify alternative candidate reinforcing steel bars for VDOT bridge decks.*

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APPENDIX A

ABBREVIATIONS

Abbreviation	Description
Al	Aluminum
C	Carbon
$Ca(OH)_2$	Calcium hydroxide
Cl^-	Chloride ion
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
Fe	Iron
L	Lateral length of corrosion
LPR	Linear polarization resistance
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Nb	Niobium
Ni	Nickel
OCP	Open circuit potential
OH^-	Hydroxide ion
ORR	Oxygen reduction reaction
P	Phosphorus
ppm	Part per million
PREN	Pitting resistance equivalency number
R_p	Polarization resistance
S	Sulfur
SCE	Saturated calomel electrode
Si	Silicon
Ti	Titanium
V	Vanadium
W	Tungsten
Wt.%	Weight percent (note: all percentages are weight based except where noted)
x	Depth of corrosion
X_{crit}	Critical corrosion depth

APPENDIX B

LONG-TERM CONCRETE EXPOSURES

A mix design with a relatively low cement content and a water-cement ratio (w/c) of 0.50 (denoted EM1) is proposed. This concrete mix is highly permeable to Cl^- ingress. Thus, relatively high concentrations of this species should develop at the rebar depth in a time frame consistent with the duration of a 2-year project. In addition, a simulated crack could be introduced into some of the EM1 specimens by placing a 0.063 in (1.6-mm-wide) stainless steel shim in the formwork centered on and perpendicular to the top mat (specimen designation EMCCON). The shim will be removed 1 day after pouring. Specimens will be fabricated in triplicate for each of the two specimen types (cracked and uncracked). Each block, as shown in Figure B.1, will be 12.0 in (30.5 cm) square and 6.0 in (15.2 cm) high with 1.0 in (2.5 cm) of concrete cover and will be reinforced by three parallel, equally spaced top mat bars and three similarly arranged bottom mat bars. Each block will be exposed outdoors for 60 days of conditioning and then outfitted with a pond for periodic wet-dry cycling and epoxy sealed on the sides. Figure B-2 shows the exposure condition for concrete samples reinforced with other rebar types that are currently being subject to the ponding cycles.

All bars in the individual blocks will be electrically connected. The cyclic wet-dry exposure will consist of 1 week wet, using a 9.1 wt.% chloride solution, and 1 week dry. During

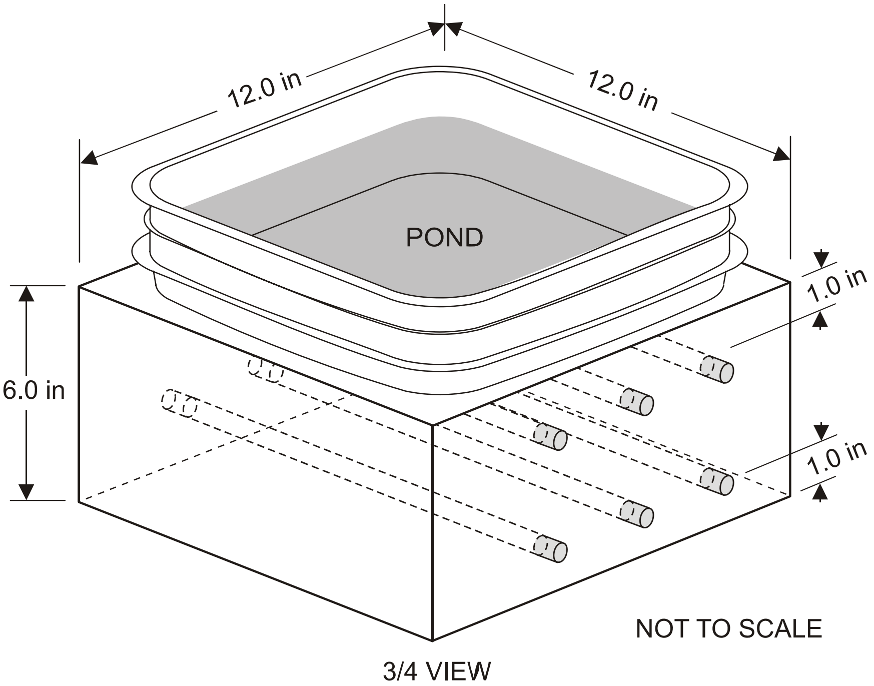

Figure B-1. Reinforced Concrete Macrocell Specimens

Figure B-2. Outdoor Exposure at Seatech of Concrete Specimens Currently Subject to Ponding Wet/Dry Cycles

the exposures, potential and macro-cell current will be routinely measured. Current density would be calculated based on the voltage drop measured across a 10-ohm resistor between the top and bottom mats (assuming uniform corrosion rate on the top mat, such that the anodic area is 70 in^2(456 cm^2).

If necessary, monitoring of the longer term concrete specimens beyond the initial 2-year period could be considered.