HIGH SILICON CAST IRON for ELECTRODES

The chemistry of high silicon cast iron for impressed current anodes is well established in Standards.
This was not always the case, because high silicon originated as an alloy for process industries. Between 1900 and World War II, the main application for high silicon cast iron was for pressure vessels and piping for acid, fertilizers and munitions. In these applications, mechanical and thermal properties were as important as corrosion resistance (1). Originally, Standard Specification ASTM A518 for Corrosion-Resistant High Silicon Iron Castings (2) reflected only process industry requirements, covering Silicon based Grade 1 and a second Grade with Chromium and Molybdenum added for strong chloride environments. In the 1950's, when Grade 1 was used for anodes in chloride conditions, the consumption rate was considered excessive. But Grade 2, containing Molybdenum, was an expensive alternative. Research began to find a more universal and economical alloy.
Chromium-containing alloys without Molybdenum exhibited superior resistance to chloride attack. Eventually, virtually all HSCI anodes in North America were manufactured to this chemistry, which was adopted as ASTM A518 Grade 3; specifically recommended for impressed current anodes. BS 1591 14 4 (3) is essentially identical; differing only in subtle ways from the ASTM A518 Gr 3 chemistry, as shown in Table 2.

Table 2: Chemical Compositions, Selected Standards

Standard	ASTM A518 GR 3		BS 1591 SiCr 14 4	
Elements	Minimum	Maximum	Minimum	Maximum
Silicon	14.20	14.75	14.25	15.25
Chromium	3.25	5.00	4.00	5.00
Carbon	0.70	1.10		1.40
Manganese		1.50		1.00
Molybdenum		0.20		
Copper		0.50		
Phosphorus				0.25
Sulphur				0.10

Discussion:

- **Silicon:** When cast iron containing appreciable silicon is consumed by corrosion, surface silicon converts to a thin passive barrier film of hydrated silica dioxide, which persists in the absence of erosion. The nominal silicon content of 14.5% was judged to provide the most attractive balance between corrosion resistance and mechanical properties, even before its application to anodes. Although silicon gives high silicon cast iron its corrosion resistance, it also embrittles it to a significant degree, particularly if metallurgical factors are not well controlled. Accordingly, Anotec has developed rigid controls for the Chill Casting process to assure consistent production of HSCI having both significantly improved impact resistance, and superior corrosion resistance. Refer to Metallic Structure (#23).
- **Chromium**: It is well established in metallurgy that alloys of iron with chromium at an atom-to-atom ratio of 7:1 "...result in a naturally occurring surface oxide which greatly improves corrosion resistance." (4)

Although early versions of high silicon iron anodes were manufactured without chromium alloy, they were consumed relatively rapidly in halide-containing environments like seawater or chloride contaminated waters[6]. During development of the HSCI, not only for anodes, various alloying elements, including molybdenum, chromium and vanadium were found to significantly reduce pitting corrosion caused by extremely corrosive, highly acidic concentrations that develop where chloride ions destroyed the silica-dioxide film By 1959, the composition based on 4.5% chromium was adopted for anodes because it gave better consumption characteristics at lower cost [6]. This alloy, patented by Durion Company of America, was trade named Durichlor 51. Eventually, when Duriron patents expired, ASTM A518 incorporated Grade 3 with 4.5% chromium content specifically for anodes. Later versions of the Standard, including ASTM A518-99 (re-approved 2003), call for chromium within the range of 3.25% to 5% for Grade 3. From a manufacturing viewpoint, foundries with modern induction melting equipment and spectrometers, are able and motivated to establish a target content within closer limits; say 4.0% to 4.5%. Unfortunately, some customer-specific specifications call for *4.5% chromium*, often without the prefix *"nominal",* or the less restrictive prefix *"minimum"*. From a manufacturing viewpoint, clauses framed with nominal values make inspection problematic. But clauses based on "minimum values" that are significantly higher than (a) the lower limits in Standards, and (b) manufacturers' target ranges, can dramatically increase production costs; not only for alloy consumption, but also for inventory investment and control. In an era of rapidly escalating alloy prices, over-consumption is costly; particularly if the customer relies on out-dated practices rather than scientific evidence and cost-benefit analysis.

- ASTM 518 Grade 3 limits **Molybdenum** to 0.2% or less even though molybdenum is beneficial to severe chloride environments. Clearly, given the higher requirement for Molybdenum in Grade 2, the limitation of Molybdenum within Grade 3 does not mean that molybdenum is deleterious to impressed anode performance. On the contrary. It follows that Molybdenum limitation is probably based on manufacturing economics, because Mo is a relatively expensive alloy that experiences wide swings in unit pricing.

  It is interesting to note that in the 1950's, when work began on alloys to improve resistance to chlorides, Molybdenum was used before chromium in the alloy "Durichlor" [6]. Later on, chromium supplanted molybdenum for economic reasons, and the alloy was named "Durichlor 51" [6].

- BS 1591, and DIN PGX70 (now obsolete), do not control molybdenum, but do limit **Sulphur** and **Phosphorous**; elements which are not referenced in ASTM A518. Sulphur and phosphorous, like lead, weaken both corrosion resistance and mechanical properties.

- ASTM A518 limits **Copper** and **Lead**, which are trace elements (along with sulphur and phosphorus) in ferrous scrap or alloys. Copper and lead can exist in cable connections in recycled anodes.

- **Copper** is not necessarily a deleterious element for anodes. In fact, for one early anode alloying development, the copper content was controlled in the range of 1% to 2% (6).
- **Lead, sulphur and phosphorous,** should be tightly controlled to low trace percentages in most ferrous castings, including anodes. The fact that these elements are not mentioned in ASTM A518 may be due to a very low failure rate of high silicon cast iron anodes. (Why legislate when no related crimes occur?)

Chemistry Requirements outside the Standard. Alloy contents outside of the established Standards are uncommon for high silicon cast iron anodes. Very occasionally however, customers will require "tightened" chemical requirements within the established standard chemistries, such as "4.5% chromium". From a manufacturing viewpoint, clauses framed with nominal values make inspection problematic. Higher or tighter than Standard alloy contents increase costs, not only for the product involved, but also for unrelated product produced during the same melt. Anodes inventories compound when alloy variations as well as anode sizes are involved. With rapidly escalating alloy prices, over-alloying or arbitrarily tight content limits, are particularly costly. Anotec is not aware of references that relate anode service life to levels of HSCI alloy content within a prescribed range of the Standards.

Mechanical Testing

A purchaser should also be aware that some mechanical requirements in the Standards may not be cost effective for anodes. ASTM A518 acknowledges this by including such phrases as: "When specified by the purchaser the...alloy shall be given a...bend test". Even so, it is recommended that purchasers acknowledge this fact by revising out-dated project specifications and purchase wording for anodes to require "*compliance with (Named Standard) chemistry*, particularly if there is no intention to have inspectors require compliance with expensive and possibly inappropriate mechanical testing requirements intended for critical engineering castings. With this in mind, a simple and inexpensive mechanical test tailored for anodes is described in Section 11: Impact Testing.

Environmental: HSCI Anodes and the Environment (#40). (Pending)

References:

1. Peacock J. H. and Cangi J.W., "High Silicon Cast Iron", Casting Engineering March, 1973 pp 35 -42.
2. Standard Specification for Corrosion-Resistant High Silicon Iron Castings, ASTM A518 - 99 (reapp.2003)
3. Specification for Corrosion Resisting High silicon Iron Castings, BS 1591:1975 (amend 1, 1995)
4. Corrosion Basics, an Introduction, NACE 1984 (p 53).
5. Laird, G. et al, Abrasion Resistant Cast Iron Handbook, AFS, 2000 (p 152)
6. Hewes F.W., "Consumption Rate Predictions Anotec High Silicon Iron (Chromium) Anodes", Caproco Ref 02-88-2309 (private correspondence) (L 48)