


Metaltech Services Limited
Station Approach
Team Valley Industrial Estate
Gateshead
NE11 0ZF

T: +44 (0) 191 3726942
E: info@msl-ltd.com
W: www.msl-ltd.com

MSL

Client:	Specialist Castings Ltd Tatham Street Sunderland Tyne & Wear SR1 2AG				
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes				
MSL Report No:	2726.17	Date:	25.03.2017	Issue No:	1
Description:	Electronic Format				
Client Ref No:	TBC				
Prepared by:	Ron Scott BSc, C.Eng, MIMMM Technical Director				
Reviewed by:	Lovlesh Beharry, MEng Engineering Manager				
Signed / Quality Stamp:	 (For and on behalf of Metaltech Services Ltd)				

This report must not be reproduced except in full, without written approval of Metaltech Services Limited. Failure to do so will result in MSL not accepting any sort of responsibility rendering the report null and void.

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	2 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Summary

Impressed Current Cathodic Protection (ICCP) plays a crucial role in the protection of vital infrastructure such as pipelines, storage tanks and structures from corrosive destruction. A popular cost effective type of semi-consumable anode used for ICCP is manufactured from high silicon cast iron (HSCI). HSCI is an acid resistant cast iron that contains 14 to 16% silicon and less than 1% carbon that has been used for over 100 years in the Chemical Industry for acid containment and processing. The initial development of high silicon cast iron dates back to 1908 **(ref 1)** and although the alloys were characterized by excellent corrosion resistance, these alloys still have known weaknesses such as low strength and toughness, high hardness and associated brittleness and cannot be hot worked or machined. Parts made from the alloy have to be made by a casting process and therefore have the associated imperfections of cast metal such as porosity and shrinkage defects.

To manufacture an anode with a high level of integrity and durability there have been several developments and innovations in the cast metal technology. These involve methods to reduce the gas content and to refine the microstructure and to refine and compact the graphite shape by the micro additions of boron and rare earth additions. In addition the application of centrifugal casting has been widely used to ensure required metal feeding and avoidance of inter-dendritic shrinkage porosity.

Since anodes are buried underground and become inaccessible for maintenance and are required to have an operational life in excess of 20 years, in addition to the developing the appropriate mechanical integrity, there is an essential requirement to validate that the anodes will have an appropriate level of corrosion resistance. A review was carried out of the various methods that have been used to assess and to validate the corrosion resistance of anodes. The main sources of information technology for this type of review are NIST, NACE International and ASTM sources of information and guidance. One of the earliest studies on Duriron (an old proprietary name for high silicon cast iron) in 1957 by the National Bureau of Standards demonstrated the successful application of a potentiodynamic method. **(ref 2)** In addition there were other approaches based on accelerated corrosion and weight loss methods. **(ref 3)**

This project was carried out to compare the corrosion performance of centrifugally cast anodes made by Specialist Castings and chill cast anodes with a sand core made by Anotec.

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	3 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Potential-dynamic tests were carried out in accordance with ASTM 59 and ASTM G5. In addition, three corrosion tests have been examined to assess their performance as accelerated tests to evaluate the anode quality and consistency.

Based on the results of the corrosion test work, the centrifugally cast anode material was found to have superior corrosion resistance. The improved corrosion resistance determined by four different methods was of the order of 20% for the hydrochloric acid test, 30% for the nitric acid electrolytic etch method and 20% for the electrolytic 3% sodium chloride test. The improvements were attributable to higher integrity cast product and lower inter-dendritic porosity. This was confirmed by metallography and measurement of relative density. The measurement of the relative density of the samples confirmed the lower levels of porosity in the centrifugally cast anode material.

Sample	SC Standard	Anotec	22 grms RE	5 grms RE
Relative Density	6.94	6.85	6.9	6.89

Table 1 Measured values of relative density

An additional indicator of the integrity of the anode material was reflected in the difficulty in the preparation of machined cross sections. The only material that permitted the preparation of a rectangular sample was the centrifugally cast material. The Anotec material cracked and fractured during the preparation of machined samples and only short samples could be prepared (Figure 1)



Figure 1 LHS= Sample machined from SC standard RHS= Sample machined from Anotec

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	4 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

1. Hydrochloric acid immersion test

The first corrosion test was based on the evidence that for semi-consumable anodes in chloride environments part of the electro-chemical reaction takes place with the associated environment. This results in the formation of chlorine and hydrogen which can combine to produce hydrochloric acid adjacent to the anode surface. Therefore the resistance to concentrated hydrochloric acid is a major corrosion resistance requirement. The test developed was to place samples of known weight and known surface area into concentrated hydrochloric acid for a period of 30 days. The results were as follows.

Sample	1 st sample	2 nd sample	3 rd sample	Average (mg/cm ² /day)
SC Standard	0.428	0.448	0.435	0.437
SC plus 5.5g RE	0.464	0.472	0.450	0.462
Anotec	0.548	0.536	0.548	0.533

Table 2 35% hydrochloric acid immersion test

The Anotec showed a dissolution rate 20% higher than the SC Standard

2. Weight loss when immersed in 10% nitric acid with a current density of 1.5ma/mm²

The second test consisted of both an applied electrical potential and chemical environment. An electrolytic etching procedure using 10% nitric acid and a current density of 1.54ma/mm² was carried out for 15 hours. The results were as follows

Sample	Weight Loss (g/m ² /h)
SC Standard	13.49
SC +5.5grms RE	17.45
Anotec	17.84

Table 3 Measurement of weight loss when immersed in 10% nitric acid with a current density of 1.5ma/mm²

The weight loss of the Anotec sample was 32% higher compared to the SC Standard sample

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	5 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

3. Consumption rate of HSCI anode as a result of continuous anodic galvanostatic dissolution at a controlled current density in 3% sodium chloride solution

The third sample was based on a weight loss after acting as an anode in a sodium chloride solution for 30 days. The weighing of the samples was carried out on the laboratory balances with capacity range of 4000 grams and the error 0,02 grams. The samples were standing on the bottom of the container during the tests and the waterline of electrolyte was kept below the electrical contact by a few centimeters. Cathodes of mild steel bar were placed either side of the anode.

The electrolyte was 3% aqueous solution of sodium chloride, prepared with distilled water and reagent grade NaCl. The volume of electrolyte was 45 L per each large sample. All samples were weighed after 30 days of anodic dissolution.

Sample ID	Weight Loss (g)	Consumption (g/A.Year)	Consumption (lb/A.Year)
SC Standard	0.7	21.1	0.047
SC Standard	0.6	18.0	0.042
Anotec	0.8	24.1	0.053
Anotec	0.8	24.1	0.053
SC + 11g RE	0.4	12.1	0.027
SC + 11g RE	0.8	24.1	0.053

Table 4 3% NaCl galvanostatic dissolution at a controlled current density

After 30days the weight loss from the Anotec anodes was 20% higher

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	6 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

1. Introduction

The anodes used for impressed current cathodic protection (ICCP) of pipelines, storage tanks and structures are based on three options, consumable, semi-consumable and non-consumable. The most popular being the semi consumable anodes and the most common type are manufactured from high silicon cast iron.

The semi-consumable anodes, such as the HSCI, as the name suggests undergo less dissolution than would be predicted by Faraday's law. This is because the anodic reaction occurs partly by oxidizing the anode (dissolution of the anode) and partly by the oxidation of the environment (with no loss of anode metal)

The initial development of high silicon cast iron dates back to the early years of 1900 and pre-date World War 1. The initial use of high silicon cast iron was for the containment of corrosive acids and the material played an important role in the manufacture of munitions used in 1914-1918 War. **(Ref 4.)**

When the high silicon cast irons contain more than 14.5% silicon the alloys are characterized by excellent corrosion resistance. However, these alloys have some known weaknesses such as low strength and toughness, high hardness and associated brittleness. Parts made from the alloy have low thermal conductivity and low thermal expansion coefficient which results in a tendency for cast metal to have porosity and shrinkage defects.

Thus the useful application of high silicon cast iron requires control of several metallurgical features during manufacture especially the microstructure. A study of the microstructure of commercial acid-resisting silicon-iron alloys has been carried out by J E Hurst and R V Riley . **(Ref 5.)** The metallographic preparation of silicon-iron-alloy specimens for metallographic examination was found to be difficult. This was due to the hardness of the iron and its proneness to inter-dendritic porosity which causes the preparation media to be trapped and the specimens become vulnerable to scratching during polishing.

The etching of the polished surface to reveal the underlying structure was also found to be difficult. Due to the acid-resistant qualities of the metal a very strong etchant had to be used. The choice of etchant was based on a mixture of hydrofluoric and nitric acid in water. However

MSL Report No:	2726.17	Page No:	7 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

for the work carried out during this project an electrolytic oxalic acid etching technique was developed.

Based on the binary equilibrium diagram for the iron-silicon system (**Ref 6**) shown in Figure 1 an alloy made with less than 15.2% silicon would be a single phase of alpha. Alloys containing over 15.2 % of silicon would be duplex and consist when in thermal equilibrium at room temperature, the alpha and epsilon phases. The epsilon phase is considered to be an intermetallic compound having the composition FeSi.

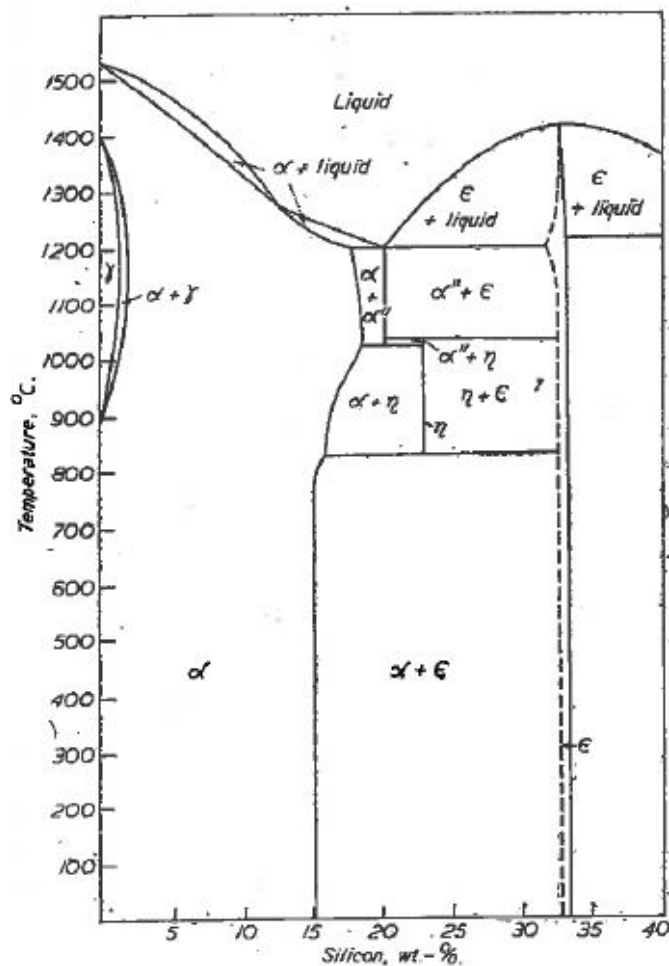


FIG. 1—Binary iron-silicon thermal equilibrium diagram according to Farquhar, Lipson, and Weill

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	8 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

The successful use of high silicon cast iron requires that the alloy to have adequate mechanical properties. These mechanical properties are dependent to large extent on the presence of free fine graphite in the microstructure. An essential aspect of the manufacture of high silicon cast iron is that they are true cast irons and contain graphite and do not solidify as steel with carbides in the microstructure.

The salient factors that provides assurance that anodes will give satisfactory service have been reviewed by Levelton Engineering Ltd (**Ref 7 and 8**) and also discussed in early Duriron patents (**Ref 9**)

Levelton Engineering Ltd examined the microstructure of HSCI samples made by sand casting, chill casting and centrifugal casting and concluded that the corrosion performance was linked with

- The shape and size and form of graphite
- The presence of secondary phases (silicides, carbides)
- The degree of segregation of alloys
- The grain size

The Duriron patent 3129095 dated May 1963, (**Ref 9**) recommended a level of mechanical strength required for anodes. The patent quotes that for high silicon cast iron a minimum transverse load value of around 800 pounds and deflection of 0.025 ins should be met to avoid excessive breakage of the anodes during handling and storage. Because normal tensile testing was difficult the patent proposed a transverse bend test. A test specimen was cast as a one inch square bar, thirteen inches long. This was placed on twelve inch centres in a testing machine, loaded at the centre until breakage occurred.

The optimum chemical analysis used for high silicon cast iron for impressed current anodes has been established over many years and are controlled by established National Standards. The alloy was initially used for anodes around 1950. Due to excessive corrosion in chloride environments anodes with a chromium addition were introduced in 1959.

2. Anode Chemical Composition

In chloride environments high silicon cast iron with molybdenum was the preferred choice but represented a relatively high cost. Eventually development work led to chromium based alloys without molybdenum which exhibited adequate resistance to chloride attack.

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	9 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Based on this development work the silicon-chromium composition became the first material of choice for high silicon cast iron anodes. This was adopted as ASTM A518 Grade 3 which was specifically recommended for impressed current anodes. BS 1591 grade 14. 4 being essentially identical to the ASTM grade differing slightly from the ASTM A518 Gr 3 chemistry, as shown in Table 2.

Table 2: Chemical Compositions, Selected Standards

Standard Elements	ASTM A518 GR 3		BS 1591 SiCr 14 4	
	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

In addition to the main elements used in the manufacture of anodes the major experienced foundries involved with anode casting are aware of other residual elements present that can have an important effect on the integrity of the product.

In addition the importance of gas content that can arise during the manufacture such as hydrogen, nitrogen and carbon dioxide. **(Ref 8)**. The importance of gas and the resulting gas porosity on the mechanical integrity of HSCI was outlined in a Duriron patent US 322161 **(Ref 9)** where the benefits of vacuum degas treatments to remove the gas was demonstrated resulting in improved mechanical integrity.

For normal castings a low hydrogen melting practice should be used (dry alloy additions and avoiding all sources of moisture) and a possibly a small addition of ferro-boron to combine with the nitrogen. US patent 3129095 recommended a boron addition to act as a grain refiner. Typical precautions against hydrogen pick-up are shown in Figure 2 **(Ref 10)**

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	10 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

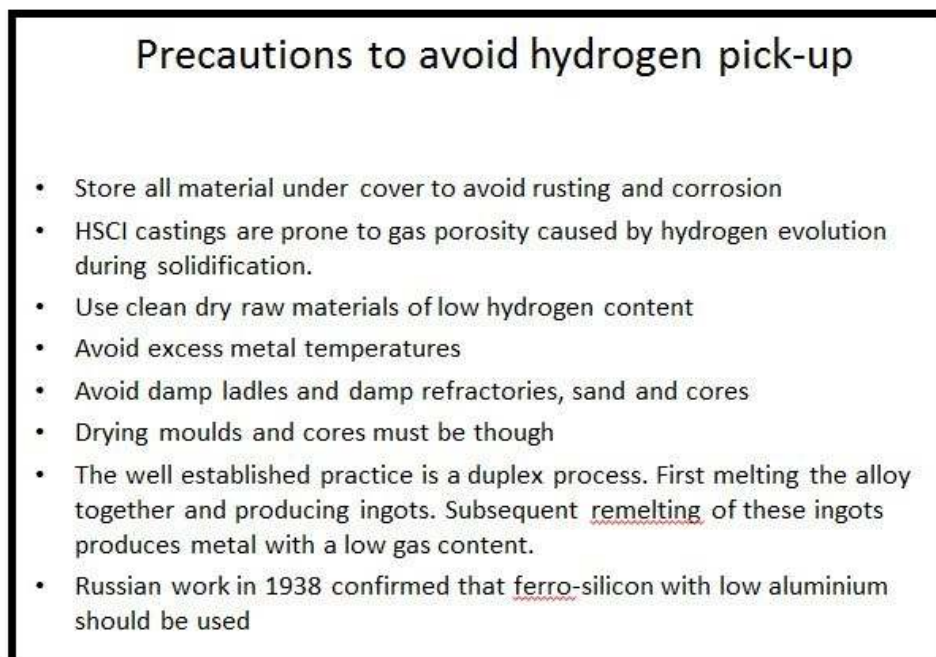


Figure 2. Typical precautions to avoid hydrogen pick-up **(Ref 10)**

Aluminium should also be kept as low as possible and therefore low aluminium ferro-silicon should be used. **(Ref 10)**

Cerium/rare earth metals have also been used to convert the flake graphite to spheroidal form. **(Ref10) (Ref 13)**. It has been shown that the addition of 0.02% of rare earth metals improved the corrosion resistance **(Ref 14)**

The trend for sulphur and phosphorous would be to target low levels. A recent European publication quoted typical levels for sulphur and phosphorous to be 0.007% and 0.1% respectively **(Ref 15)**

3. Production methods compared

High silicon cast irons can be cast by several of the established casting processes, for example sand casting, investment casting, permanent mould chill casting and centrifugal casting. The various casting processes all compete in terms of price and delivered quality and the choice of

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	11 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

the "best" casting process for high silicon cast iron anodes has to be made by the steel foundry.. The processes which have gained acceptance for the manufacture of high silicon cast iron are based on the integrity requirements and the casting process that will give parts that are "fit for service". These processes are either centrifugal casting or chill casting with a shell core. Both processes are known to have the process capability to cast tubular impressed current anodes which have to meet strict radiographic quality levels in accordance with ASTM E186.

However based on many years of experience many users specifically specify centrifugal casting. For example a data sheet published by BAC states "BAC silicon iron tubular anodes are centrifugally cast" (**Ref 16**)

The three main established casting processes for tubular impressed current anodes that are often compared and contrasted in terms of advantages and disadvantages are:

- Centrifugal casting
- Chill casting with a sand core
- Sand casting with a core

It has been proven that sand casting can be regarded as a sub-standard process for the casting of high silicon cast iron for the manufacture of anodes and will therefore not be compared in this evaluation.

This report compares the metallurgical examination of samples from parts cast by the "metal mould methods". The includes the centrifugal casting (SC Samples)and the chill casting with a shell sand core. (Anotec samples).

3.1. Centrifugal casting

Centrifugal casting is a relatively old casting method the first industrial use of was the manufacture of cast iron pipes in 1848.

Centrifugal casting uses a permanent mould that is rotated about its axis at a speed between 300 to 3000 rpm as the molten metal is poured. Centrifugal forces cause the metal to be pushed out towards the mould walls, where it solidifies after cooling. The centrifugal force assists with the feeding of the casting and therefore avoids shrinkage porosity.

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	12 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Using centrifugal casting avoids most of the casting defects associated with static casting such as internal shrinkage, gas porosity and non-metallic inclusions.

The metal distribution and the solidification of the metal in the centrifugal casting process has several advantages.

The liquid metal solidifies through the removal of heat and with centrifugal casting the heat is removed through contact with the metal mould. Therefore, as the molten metal is forced into contact with the surface of a spinning mould, due to centrifugal forces, the molten metal transfers heat into mould surface relatively quickly and solidification starts as a thin layer at the outside diameter and the solidification progresses toward its hollow centre.

The directional solidification creates several advantages. It eliminates the possibility of air and gas being trapped in the casting and reduces the risk of gas porosity. It also eliminates shrinkage defects, which can occur in all other casting processes because molten material contracts as it solidifies. When this occurs in centrifugal casting, more molten metal is forced under the centrifugal force and feeds the areas of potential shrinkage porosity. In addition the centrifugal casting process also limits inclusion defects. Potential non-metallic inclusions are generally lighter than molten metal and, they will be forced to the inside diameter of the casting. Another advantage of the centrifugal casting process is related to reduced segregation and the formation of fine grained microstructures. This results from the solidification structure of a centrifugal component being near perfect directional solidification from the outside inward, and grain growth that is typically columnar resulting in a fine grain size.

Hot tears have to be avoided since they can be developed in centrifugal castings when it runs at the highest rotation speeds. This is avoided by the slow build-up of speed. Longitudinal tears may also occur when contraction of casting combined with the expansion of the mould, generates hoop stresses exceeding the cohesive strength of the metal at temperatures in the solidus region. Casting development work is carried out to optimise the casting parameters.

3.2. **Chill casting:**

The mould used for chill casting consists of two halves that are made of metal, usually cast iron or steel. The cavity, including the runners and gating system are machined into the mould halves. Shell core are used to allow the manufacture of the hollow anodes.

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	13 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Prior to casting the mould surface is covered with a spray of graphite or silica, which acts as a lubricant which improves the life of the mould. In addition the mould coating improves the flow of the liquid metal, and it allows the cast part to be withdrawn from the mould more easily. The casting process needs to be optimised to avoid the casting defects such as internal shrinkage, gas porosity and non-metallic inclusions and hot cracking

4. Evaluation

Visual examination confirmed the higher integrity of the surface and the bore obtained by the centrifugal process. As described above the centrifugal casting process has several advantages that result in consistent and good levels of integrity. However, the chill cast process is vulnerable to casting defects such as internal shrinkage, gas porosity and non-metallic inclusions and hot cracking. Anotec Industries data sheet confirms that chill cast method requires strict control with a statement that *"the process is sensitive, and process control is extremely important"* (Ref 17)

The metallographic work confirmed that the centrifugally cast sample had a finer graphite and much lower porosity probably due to the high cooling rate and centrifugal force allowing better feeding during solidification.

The chill cast showed coarser graphite, larger porosity and cracks. .

Based on the results of the corrosion test work the centrifugally cast anode material was found to have superior corrosion resistance. The improved corrosion resistance determined by four different methods was of the order of 20% and was attributable to higher integrity cast product and lower inter-dendritic porosity. This was confirmed by metallography and measurement of relative density. The measurement of the relative density of the samples confirmed the lower levels of porosity in the centrifugally cast anode material.

Sample	SC Standard	Anotec	22 grms RE	5 grms RE
Relative Density	6.94	6.85	6.9	6.89

Table 1 Measured values of relative density

An additional indicator of the integrity of the anode material was reflected in the difficulty in the preparation of machined cross sections. The only material that permitted the preparation of a rectangular sample was the centrifugally cast material. The Anotec material cracked and

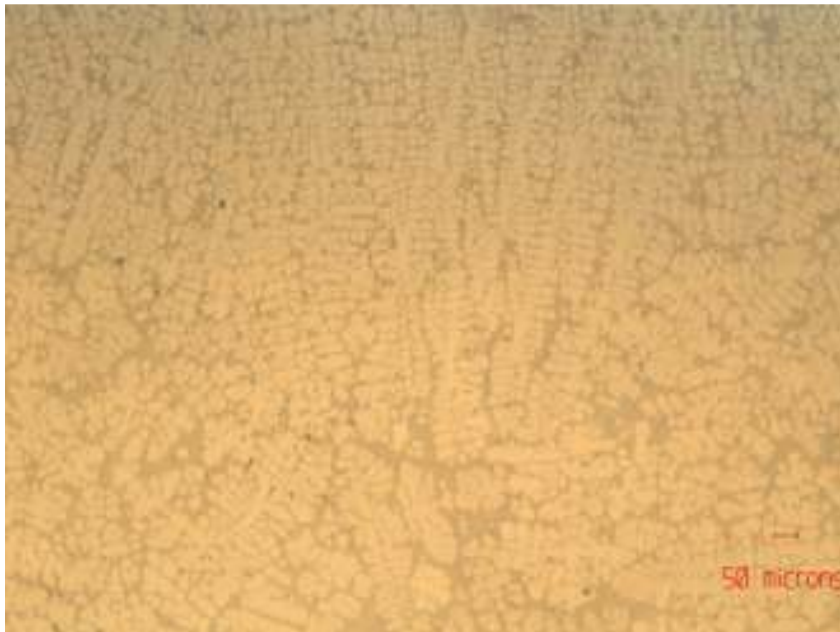
<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	14 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

fractured during the preparation of machined samples and only short samples could be prepared (Figure 1)



Photo 1 LHS= Sample machined from SC standard RHS= Sample machined from Anotec

Photo 2 Centrifugal casting. Showing fine graphite (dark areas) in a single alpha phase
Magnification approximately X50

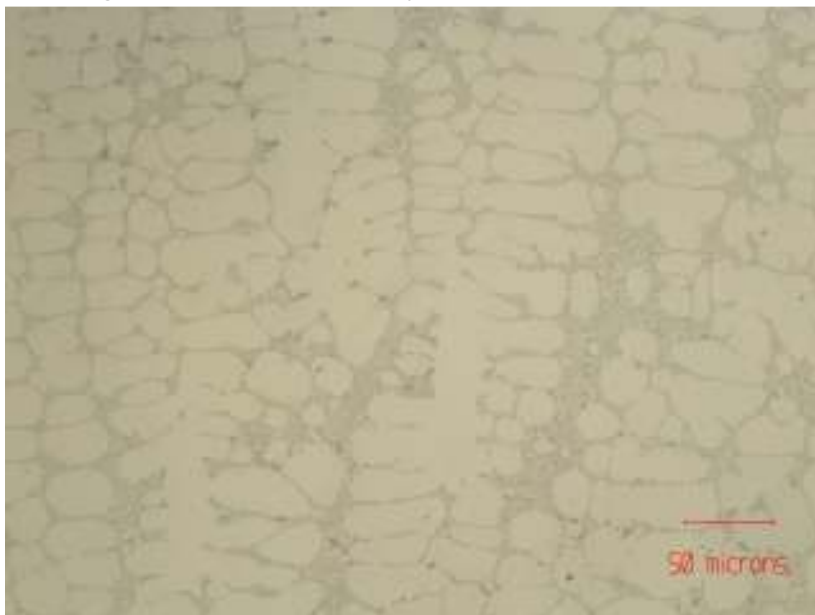


<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	15 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Photo 3 Centrifugal casting. Showing fine graphite (dark areas) in a single alpha phase
Magnification approximately X100



Photo 4 Centrifugal casting. Showing fine graphite (dark areas) in a single alpha phase
Magnification approximately X200



<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	16 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Photo 5 Centrifugal casting. Showing fine graphite (dark areas) in a single alpha phase
Magnification approximately X500

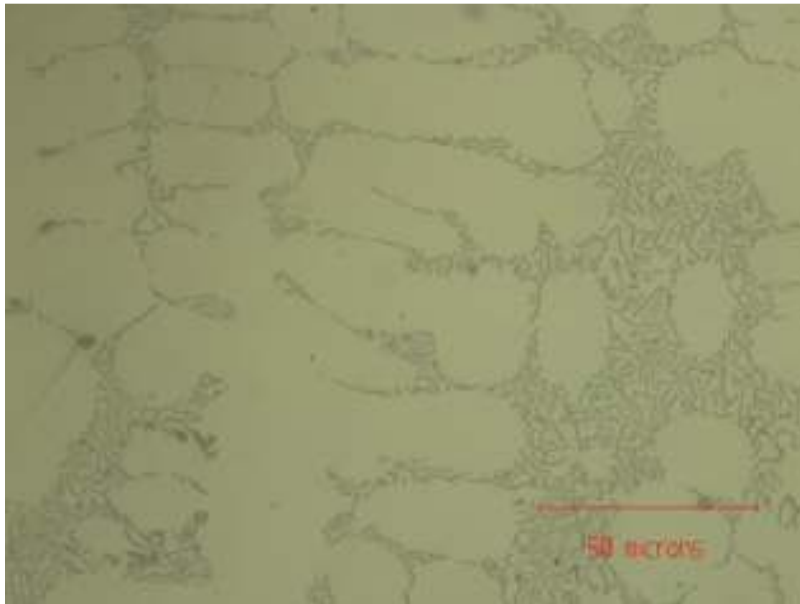


Photo 6 Chill cast showing porosity. Showing fine graphite (dark areas) in a single alpha phase
(light areas) with porosity showing black. Magnification approximately X50



<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	17 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Photo 7 Chill cast showing porosity. Showing fine graphite (dark areas) in a single alpha phase (light areas) with porosity showing black.. Magnification approximately X100

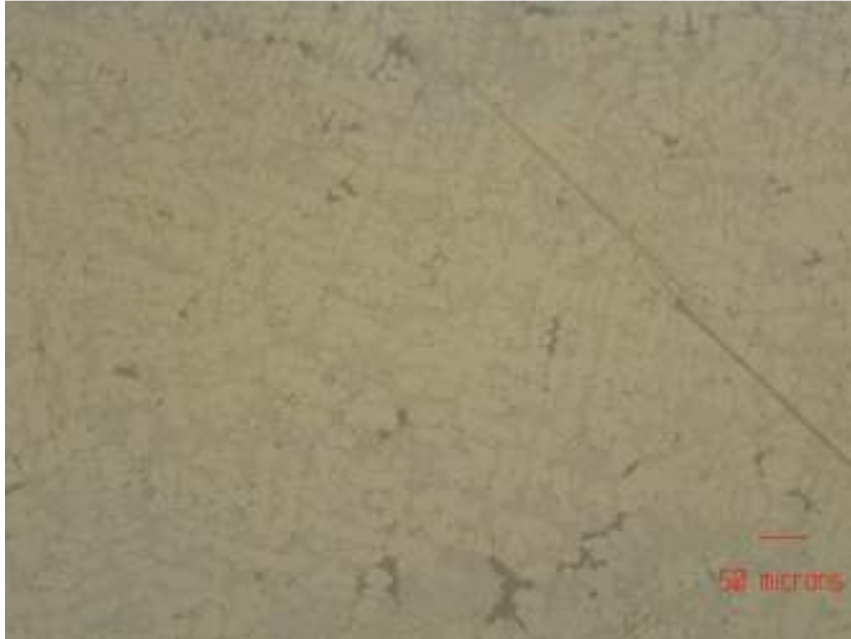
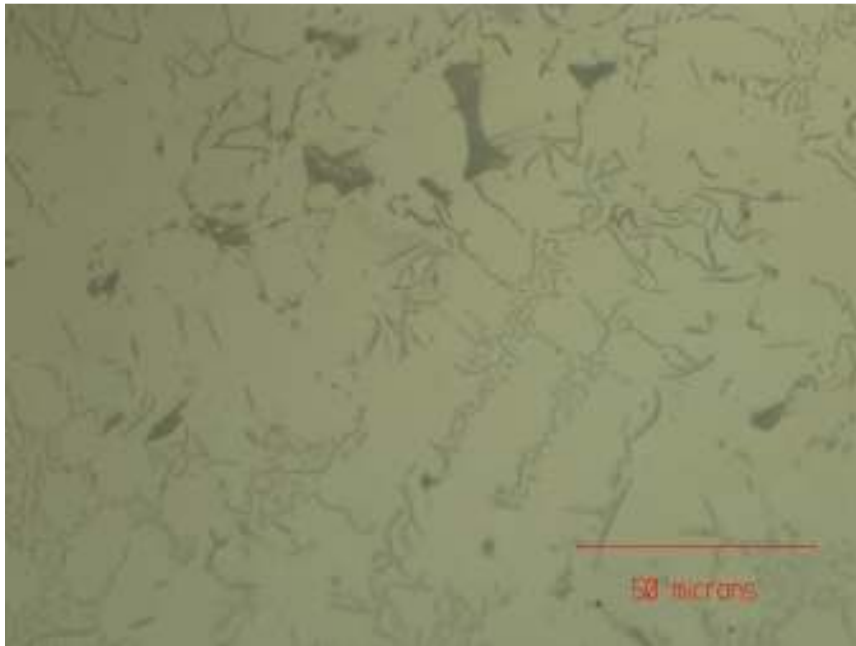


Photo 8 Chill cast showing porosity. Showing fine graphite (dark areas) in a single alpha phase (light areas) with porosity showing black. Magnification approximately X200



<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	18 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Photo 9 Chill cast showing porosity. Showing fine graphite (dark areas) in a single alpha phase (light areas) with porosity showing black. Magnification approximately X500



5. Corrosion Testing

5.1. Hydrochloric acid immersion test

The first corrosion test was based on the evidence that for semi-consumable anodes in chloride environments part of the electro-chemical reaction takes place with the associated environment. This results in the formation of chlorine and hydrogen which can combine to produce hydrochloric acid adjacent to the anode surface. Therefore the resistance to concentrated hydrochloric acid is a major corrosion resistance requirement. The test developed was to place samples of known weight and known surface area into concentrated hydrochloric acid for a period of 30 days. The results were as follows.

Sample	1 st sample	2 nd sample	3 rd sample	Average (mg/cm ² /day)
SC Standard	0.428	0.448	0.435	0.437
SC plus 5.5g RE	0.464	0.472	0.450	0.462
Anotec	0.548	0.536	0.548	0.533

Table 2 35% hydrochloric acid immersion test

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	19 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

The Anotec showed a dissolution rate 20% higher than the SC Standard

5.2. Weight loss when immersed in 10% nitric acid with a current density of 1.5ma/mm²

The second test consisted of both an applied electrical potential and chemical environment. An electrolytic etching procedure using 10% nitric acid and a current density of 1.54ma/mm² was carried out for 15 hours. The results were as follows

Sample	Weight Loss (g/m ² /h)
SC Standard	13.49
SC +5.5grms RE	17.45
Anotec	17.84

Table 3 Measurement of weight loss when immersed in 10% nitric acid with a current density of 1.5ma/mm²

The weight loss of the Anotec sample was 32% higher compared to the SC Standard sample

5.3. Consumption rate of HSCI anode as a result of continuous anodic galvanostatic dissolution at a controlled current density in 3% sodium chloride solution

The third sample was based on a weight loss after acting as an anode in a sodium chloride solution for 30 days. The weighing of the samples was carried out on the laboratory balances with capacity range of 4000 grams. The samples were standing on the bottom of the container during the tests and the waterline of electrolyte was kept below the electrical contact. Cathodes of mild steel bar were placed either side of the anode.

The electrolyte was 3% aqueous solution of sodium chloride, prepared with distilled water and reagent grade NaCl. The volume of electrolyte was 45 L per each large sample. All samples were weighed after 30 days of anodic dissolution.

MSL Report No:	2726.17	Page No:	20 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Sample ID	Weight Loss (g)	Consumption (g/A.Year)	Consumption (lb/A.Year)
SC Standard	0.7	21.1	0.047
SC Standard	0.6	18.0	0.042
Anotec	0.8	24.1	0.053
Anotec	0.8	24.1	0.053
SC + 11g RE	0.4	12.1	0.027
SC + 11g RE	0.8	24.1	0.053

Table 4 3% NaCl galvanostatic dissolution at a controlled current density

After 30days the weight loss from the Anotec anodes was 20% higher

5.4. Potentiodynamic Testing

Potential-dynamic test were carried out in accordance with ASTM 59 and ASTM G5.

5.4.1. ASTM G59

CALCULATION OF CORROSION RATES FROM POLARIZATION DATA

The corrosion current can be calculated from the corrosion potential and the thermodynamic potential if the equation expressing polarization of the anode or cathode is known, and if the anode – cathode area ratio can be estimated.

Stern and Geary [8] derived the very important and useful equation, now known as the Stern – Geary equation

$$I_{\text{corr}} = \frac{I_{\text{appl}}}{2.3\Delta\phi} \left(\frac{\beta_c\beta_a}{\beta_c + \beta_a} \right)$$

$$I_{\text{corr}} = \frac{1}{2.3R} \left(\frac{\beta_c\beta_a}{\beta_c + \beta_a} \right)$$

where β_c and β_a refer to Tafel constants for the cathodic and anodic reactions, respectively, and $I_{\text{appl}} / \Delta\phi$ is the polarization slope (the reciprocal of the polarization resistance, $R = \Delta\phi / I_{\text{appl}}$) in the region near the corrosion potential, for which the change of potential, $\Delta\phi$, with I

MSL Report No:	2726.17	Page No:	21 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

appl is essentially linear. Under conditions of slight polarization, for which $\Delta \phi$ is not more than about 10 mV, the anode – cathode area ratio, which need not be known, remains essentially constant and conditions otherwise at the surface of the corroding metal are largely undisturbed.

The general validity of these equations is shown by data summarized in Figure x The observed corrosion current, corresponding to data on corrosion of nickel in HCl and on corrosion of steels and cast iron in acids and in natural waters, extends over six orders of magnitude.

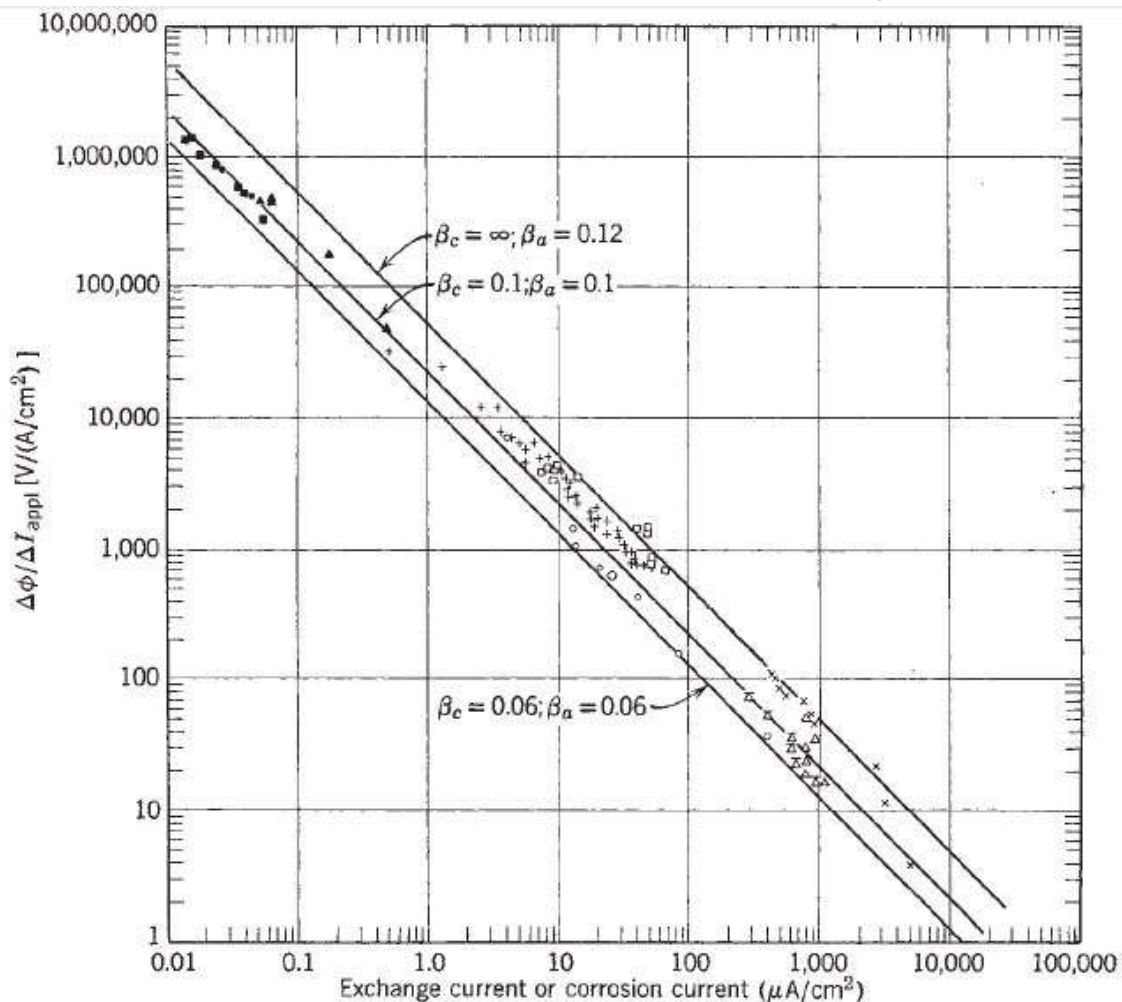
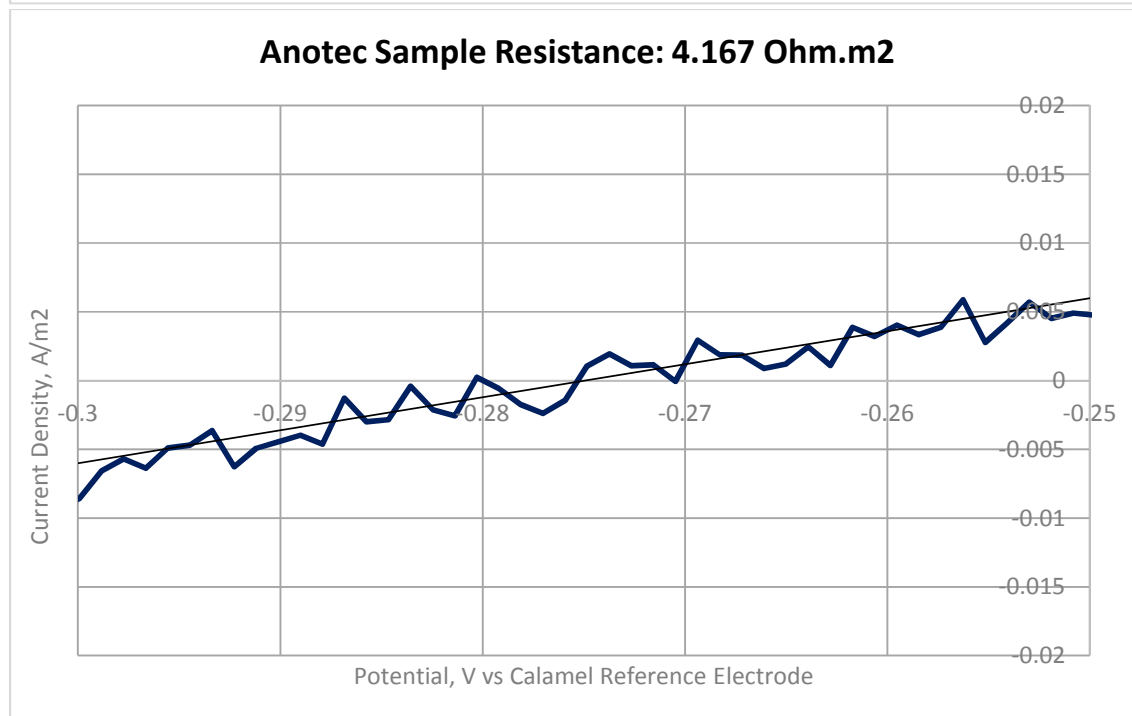
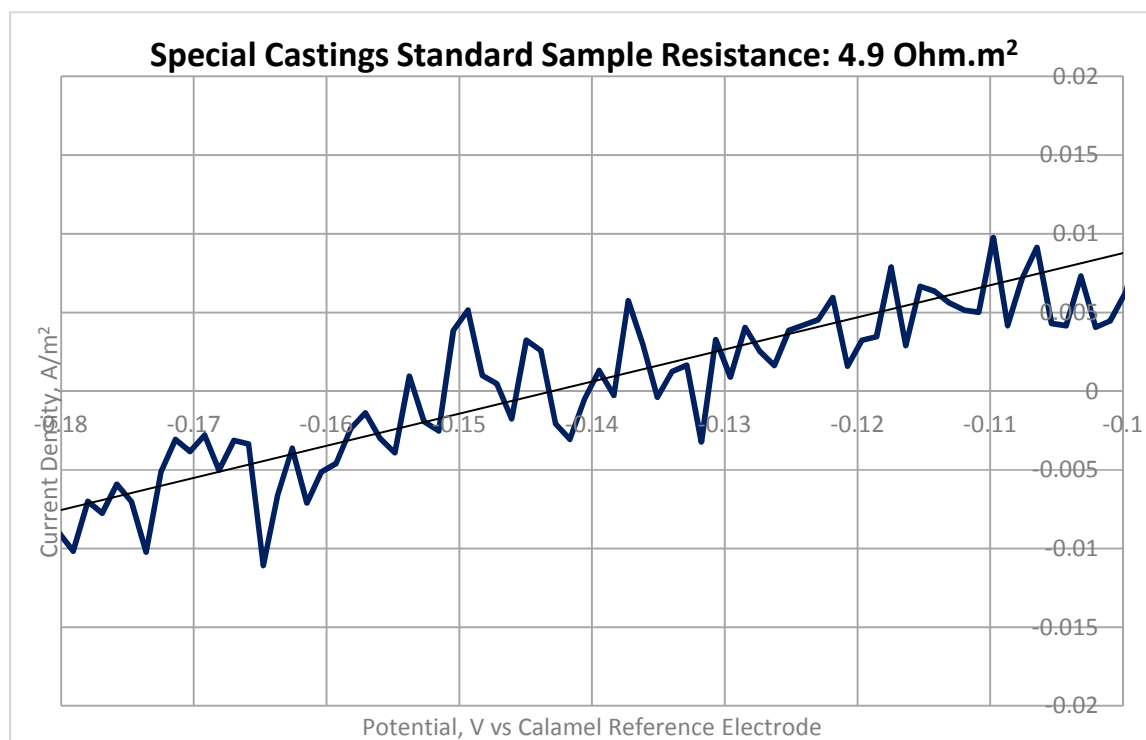
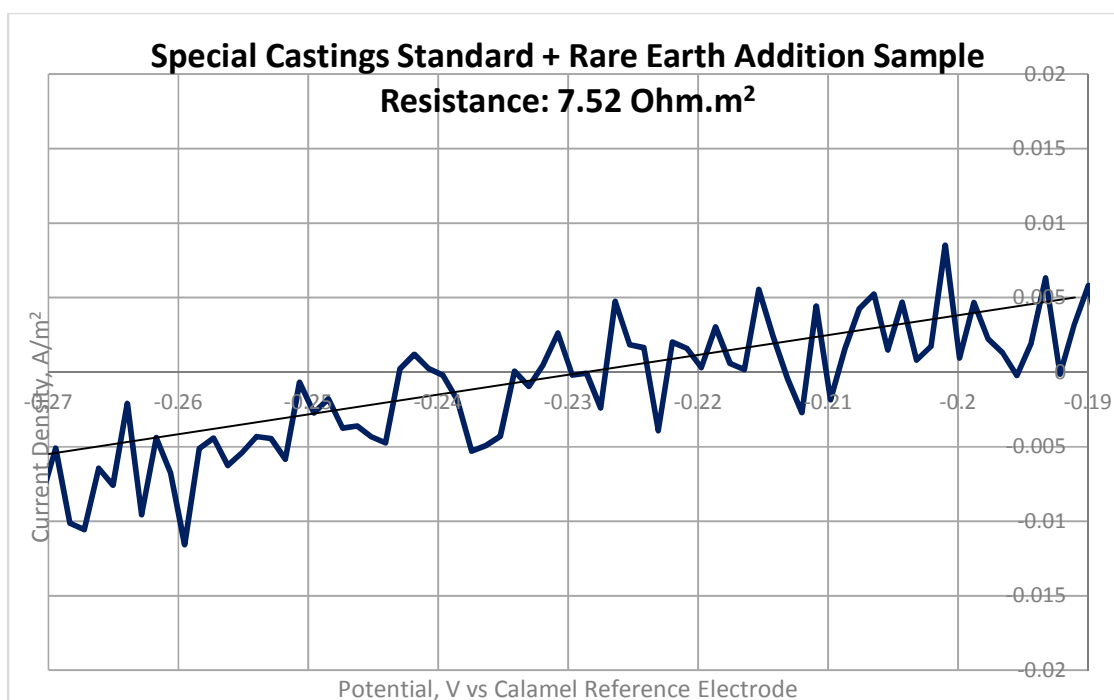
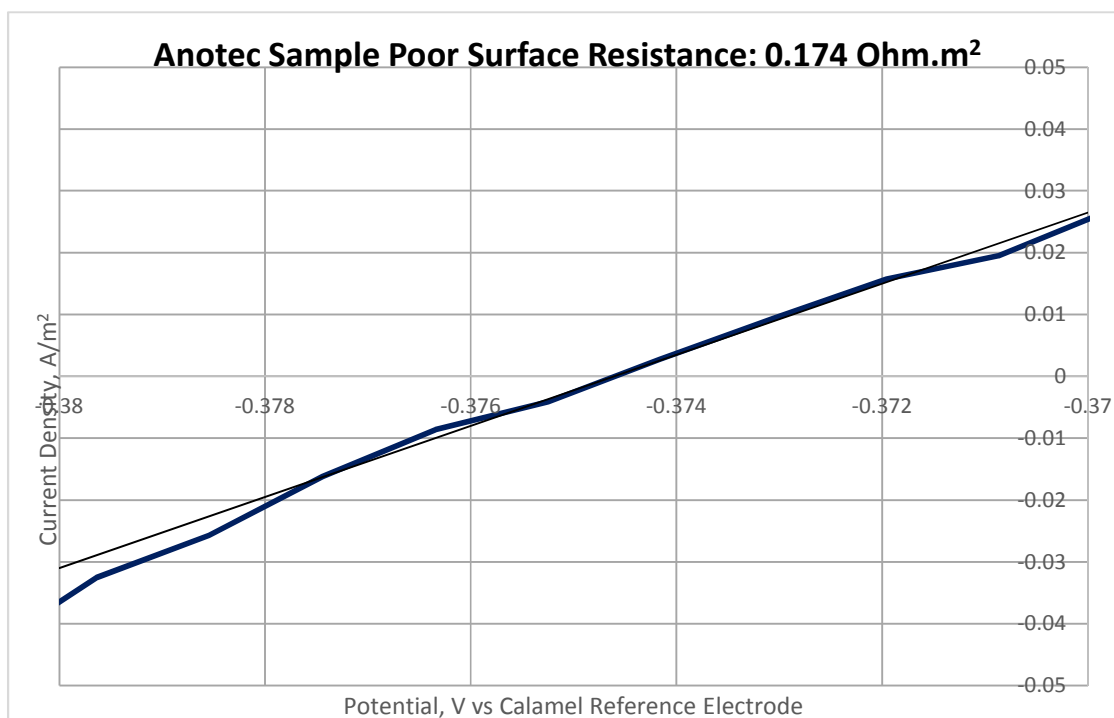


Figure 3. Relation between polarization slope at low applied current densities and observed corrosion or exchange current densities [9]. (Copyright ASTM INTERNATIONAL. Reprinted with permission.)

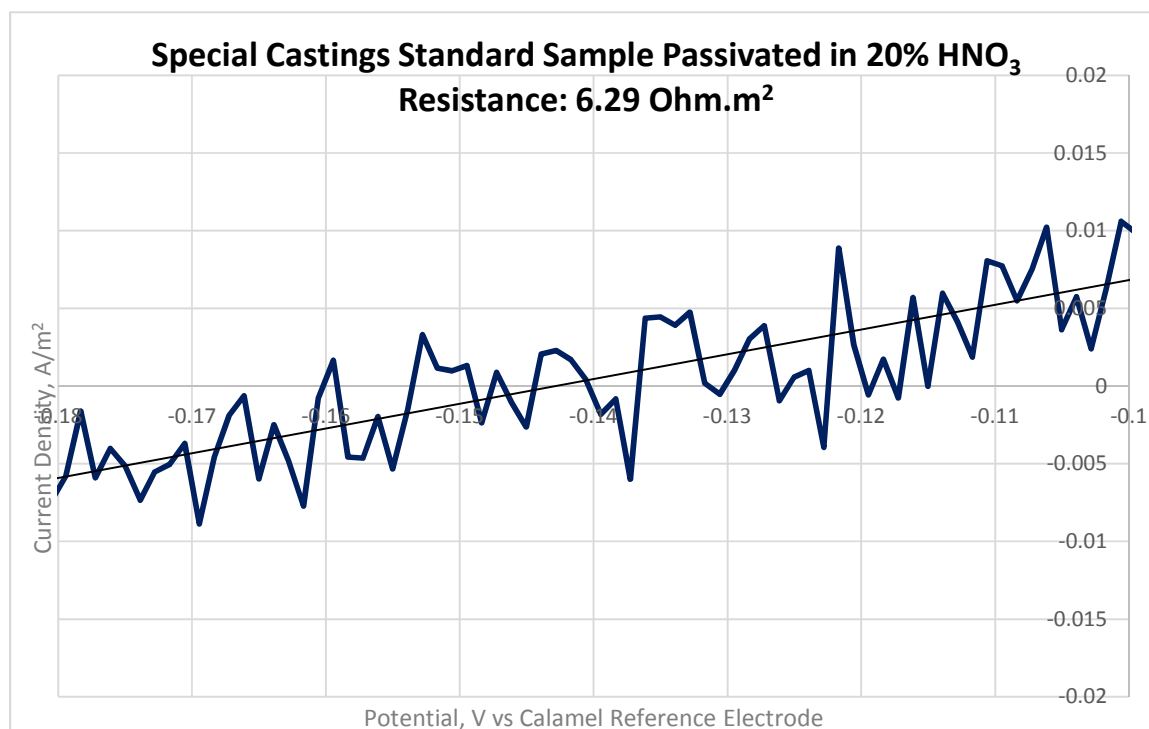
MSL Report No:	2726.17	Page No:	22 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			



MSL Report No:	2726.17	Page No:	23 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			



MSL Report No:	2726.17	Page No:	24 of 28	MSL
Prepared by:	Ron Scott	Date:	25.03.2017	
Client:	Specialist Castings Ltd	Issue No:	1	
Title:	Metallurgical development and product evaluation of high silicon cast iron tube anodes			



Open Circuit Potential	
	OCP (V)
Standard SC	-0.266
SC + 5.5g RE	-0.209
SC + 22g RE	-0.223
Anotec	-0.175

5.4.2. ASTM G5

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	25 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

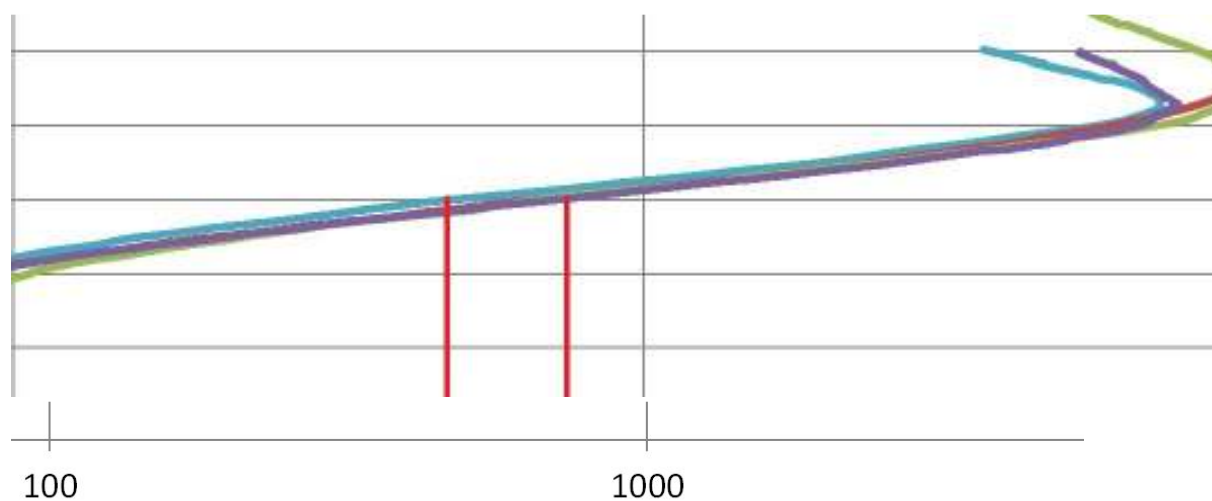
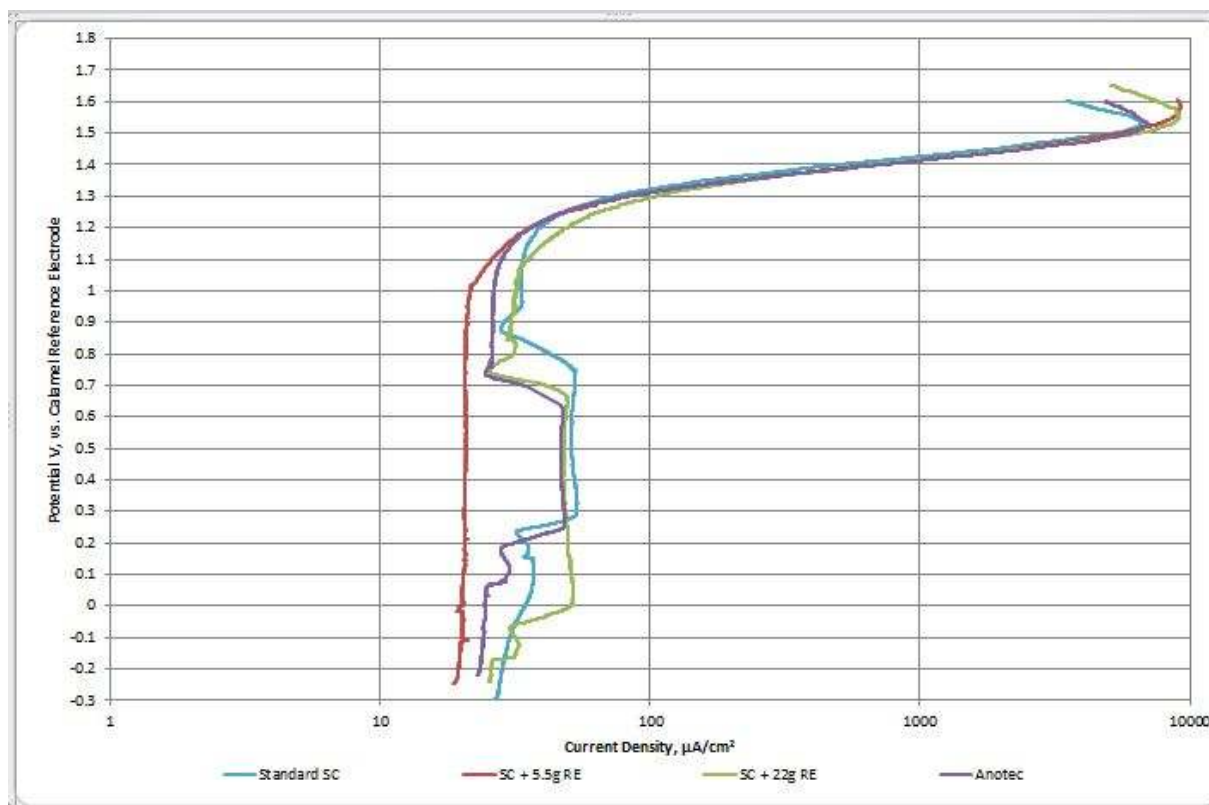
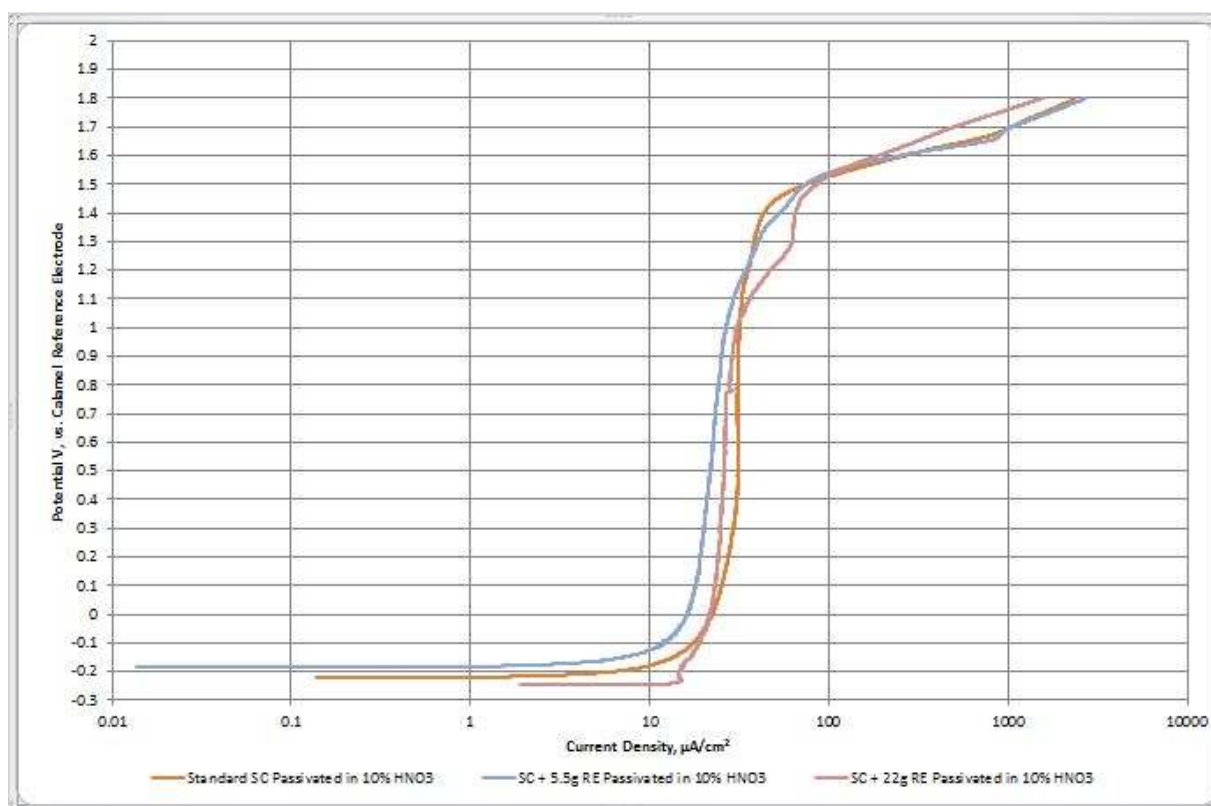


Figure 4 Due to the log scale the apparent small difference represents a large current change

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	26 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

Effect of passivation in nitric acid.

A procedure used to improve the corrosion resistance of stainless steels is passivation in nitric acid. Since the corrosion resistance of the HSCI depends upon the formation of a passive scale of Si and Cr a passivation treatment was carried out to establish if it improved the corrosion resistance.



Open Circuit Potential

	OCP (V)
SC Standard Passivated	+0.660
SC + 5.5g RE Passivated	+0.752
SC + 22g RE Passivated	+0.734

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	27 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

References

1. Trygve D Yensen : Magnetic and other properties of iron-silicon alloys melted in vacuum. University of Illinois Bulletin 83 Vol XIII November 1915.
2. W J Schwerdtfeger: Journal of Research of National Bureau of Standards. Vol 58 No 3 March 1957. RP 2746
3. A.V. Goncharov et al: Electrochemical Behavior of Fe-Si Impressed Current Anodes Testing. NACE Corrosion 2013 Paper Number 2309
4. Duriron and Durichlor 51M Materials Dat Sheet. Flowserve.
https://www.flowserve.com/files/Files/Literature/FPD/bulletin_a2.pdf
5. J E Hurst and R V Riley: The microstructure of commercial acid-resisting Silicon-Iron Alloys; Journal of the Iron and Steel Institute, 155, 172-178 (Feb 1947)
6. M. C. M. Farquhar, H. Lipson and A. R. Weill : Journal, of the Iron and Steel Institute. 1945, NoII .p. 457
7. R.S. Chariton,, BH Levelton & Associates, Richmond, B.C. Canada : Effect of Microstructure on the Corrosion Resistance and Mechanical Properties of High Silicon Cast Iron Anodes . <http://www.farwestcorrosion.com/technical-paper-effect-of-microstructure-on-high-silicon-cast-iron>
8. www.anotec.com/articles/.../Art-23-Metallic-Structure-for-HSCI-Anodes-Rev01.pdf
9. US Patent 3129095 May 1963
10. ASM Specialty Handbook Cast Iron Page 151
11. US {Patent 3222161 December 1965
12. H T Angus Cast Irons Physical and Engineering properties . Butterworths 1976
13. Chinese Patent CN 103146989A. Centrifugal casting method of chromium containing high silicon cast iron anode tubes
14. Li Ju-cang et al: Corrosion properties of high silicon iron based alloy in nitric acid, China Foundry. Vol 14 No4 p276.
15. Veselinka Dordovic et al: Corrosion resistant high silicon cast iron, Proceedings of 3rd BMC-2003 Macedonia p333
16. <http://www.bacgroup.com/Global/BAC/CP%20Catalogue/1.4.1%20SiFe%20Anode%20Standard.pdf>
17. Production Methods for HSCI Anodes: Sand, Centrifugal and Chill Casting. Anotec Industries

<i>MSL Report No:</i>	2726.17	<i>Page No:</i>	28 of 28	MSL
<i>Prepared by:</i>	Ron Scott	<i>Date:</i>	25.03.2017	
<i>Client:</i>	Specialist Castings Ltd	<i>Issue No:</i>	1	
<i>Title:</i>	Metallurgical development and product evaluation of high silicon cast iron tube anodes			

- End of report-