

Graphitic corrosion of a cast iron trunk main: implications for asset management

R. Logan¹, M. J. Mulheron¹, D. A. Jesson¹, P. A. Smith¹,
T. S. Evans², N. Clay-Michael² & J. T. Whiter³

¹*Faculty of Engineering and Physical Sciences, University of Surrey, UK*

²*Innovation, Thames Water Utilities Ltd, UK*

³*Formerly of Innovation, Thames Water Utilities Ltd, UK*

Abstract

Failures of (large diameter) cast iron trunk water mains can be catastrophic in the damage they can cause and it is therefore imperative to understand how cast iron deteriorates in order to help predict those areas of a water supply network which are at greatest risk of failure. Cast irons undergo a localized form of corrosion known as graphitic corrosion. Although a well reported phenomena, the mechanisms of graphitic corrosion are not fully understood. Scanning electron microscopy, in conjunction with energy dispersive x-ray spectroscopy, was used to characterise the microstructure and chemistry of the graphitic corrosion that occurs on the external surface of the pipe during time in service. It was found that the graphite flakes within the cast iron are deteriorating during the corrosion process. High levels of chlorides are often found at the corrosion interface, within graphitic pits in the pipe wall. The implications of these observations on the development of models used to predict the remaining service life of buried trunk main are discussed.

Keywords: corrosion, cast iron, water distribution, chlorides, trunk main.

1 Introduction

For over 150 years, grey cast iron was the material of choice for the construction of water distribution systems in the United Kingdom. Over the past few decades new materials have been introduced and cast iron pipe is slowly being phased out from the water distribution network [1]. Despite this, much of the existing potable water infrastructure is still constructed from cast iron pipe of various



ages, diameters and jointing systems. A significant portion of current pipe networks are comprised of aging cast iron infrastructure that can be up to 150 years old [2, 3]. Even after many years of service much of this cast iron infrastructure still remains in a satisfactory condition for continued use, however there is an increasing risk of these pipes failing as a result of material loss due to corrosion. Pipe weakened by corrosion may result in unwanted leakage from the pipe. In the very worst case scenarios, the results of the failure of a large diameter trunk main can result in large scale interruptions to water supplies, flood damage, transport disruption, expensive repair costs, brand damage and even injury [4].

2 Graphitic corrosion of cast iron

Grey cast irons undergo a unique form of deterioration, known as graphitic corrosion. It is commonly held that in this form of corrosion graphitic corrosion, the ferritic iron component in the alloy goes into solution leaving behind a porous residue consisting of graphite flakes interspersed with iron oxides and other insoluble products such as siliceous compounds and phosphide eutectic stringers [5]. At its simplest this may be considered an example of a local galvanic corrosion cell with the ferrous metal becoming anodic (and hence passing into solution) relative to the graphite flakes and other phases in the microstructure.

It is an important observation in trunk main, that graphitic corrosion is highly localised, with significant variation in the depth of penetration at the sub metre scale [3]. It is common to find a severely corroded section of pipe adjacent to uncorroded cast iron (Figure 1).

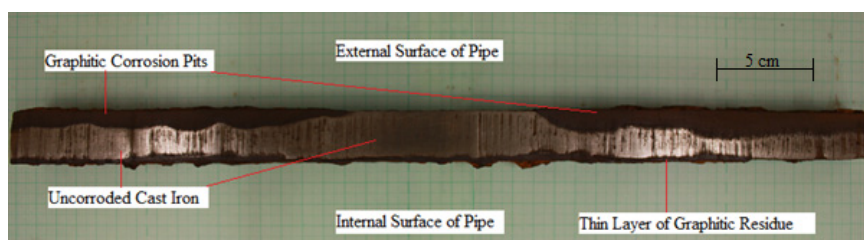


Figure 1: Section of corroded cast iron trunk main.

The graphitic residue preserves the original shape of the corroded pipe, to the extent that the original mill markings on the pipe may still be exhibited. However, the graphitic residue is structurally weaker than the original cast iron which it replaces, reducing the capacity of the pipe to carry an in-service load [6]. Left undisturbed a deteriorated pipe can continue to function, provided the service stresses are constant or small. However, the weakened pipe is vulnerable to mechanical failure as a result of ground movements, pressure changes or cyclic loading acting upon the reduced section of the metal within the structure.

There are several ways that graphitic corrosion can manifest itself. Most commonly a thin surface layer of graphitic residue forms on the exterior surface of the pipe, resembling the 'icing' on a cake. This layer of graphitic residue with its intermixed insoluble corrosion products can potentially act as an impermeable coating, protecting the pipe from further corrosion and significantly reducing the rate of corrosion. In such cases it is possible to predict the residual strength of the corroded pipe based on a loss of section approach [7].

At other times, the graphitic corrosion may be in the form of a pit, or series of pits, that develop in the pipe wall and rather than acting as benign surface layer the graphitic corrosion process may continue through the whole wall thickness of the pipe. Such pits can be referred to as 'icicles'. Unlike 'icing' a loss of section is not appropriate; instead a fracture mechanics approach treats these as cracks in the pipe surface [3].

The localized, unpredictable and complex nature of the graphitic corrosion process makes it difficult to develop models that predict the remaining useful life of a cast iron pipe that has been in the ground for several decades. Although it has been observed that cast iron is more vulnerable to severe corrosion when buried in certain soil conditions; especially soils such as clay soils [8, 9].

It is by no means certain that a cast iron pipe will corrode severely in such aggressive soils; other factors, such as moisture content and the presence of a surface coating, can also play a significant role [10].

Graphitic corrosion is known to occur in salt waters, acidic mine waters, dilute acids, underneath iron tubercles, in soils with a high moisture content such as saturated clays, soils containing chlorides from deicing salts or seawater, and in the presence of sulphate reducing bacteria. [5, 11–13]. Soils are a complex environment, and it is therefore difficult to conclude exactly which parameter is most likely to result in severe corrosion [14].

The basic electrochemical model of the corrosion of buried iron pipe is that metal loss is directly proportional to the flow of direct current from cathodic sites on the metal surface to anodic sites, with the soil acting as an electrolyte. The amount of dissolved inorganic solutes (anions and cations) in water or soil is directly proportional to the solution electrolytic conductivity [10, 15]. High moisture content and soluble salts will both serve to lower the resistivity of a soil. A recent study on leaks of cast iron pipe versus soil resistivity, show an exponential increase in the number of leaks occurring in soils with resistivities of 3000 ohm cm and below [15]. It has been observed that soils high in carbonates can lead to a protective layer forming on the metals surface, while soils with a high chloride content, are notably corrosive, due to lowered resistivity and inhibition of passivation of the metal surface [16]. The normal range for chlorides in soils is between 50 and 200 mg/kg [17] However chloride concentrations as high as 10,000 mg/l have been recorded in the roadside water runoff after road de-icing [18]. For reference, seawater is 20,000 mg/l.

3 Preparation of samples for microscopy

Specimens were sourced from nine ex-service water mains that had been examined as part of a previous study [7]. Eight of these nine pipes had failed in service. The pipe wall thickness of these samples was in the range 30–40 mm. The pipe samples had previously been sectioned into plates nominally 300 mm x 300 mm x 30–40 mm. Small samples, approximate dimension 10 mm x 10 mm x 35–40 mm were cut from the plates. The samples were then prepared so that a cross sectional face of the pipe could be studied in a scanning electron microscope (SEM) (Figure 2). The samples were mounted in resin, then ground mechanically using SiC papers (grade 80–4000), and polished with diamond paste (6, 3 and 1 μm) and finally with 0.25 μm colloidal silicon.

A Hitachi 3200N scanning electron microscope (accelerating voltage: 20 keV), directly coupled to an energy dispersive spectroscopy (EDX) detector was used for microstructural and chemical investigations of the samples. All SEM images presented in this paper were taken using the back scattered detector with the exception of Figure 6 which is a secondary electron image.

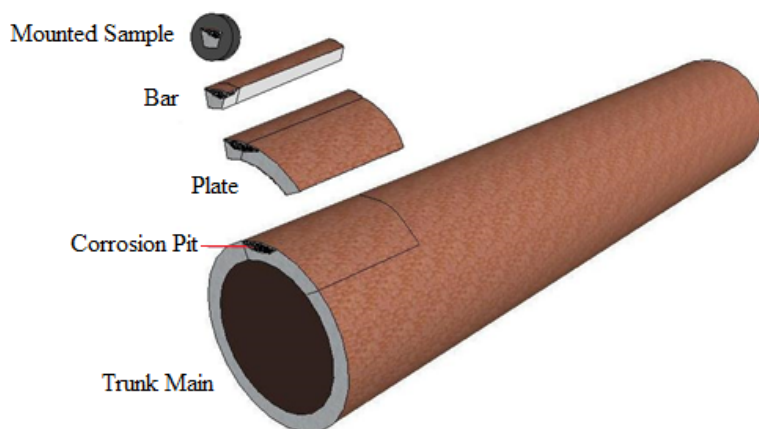


Figure 2: Schematic illustrating how a 48" diameter trunk main is sectioned for investigation.

4 Results and discussion

Of the nine pipes that were available for sampling graphitic corrosion was found on the external surface of seven. The extent of corrosion varied from "moderate", where the maximum depth of corrosion was less than 10% of the original wall thickness, to "very severe", where the maximum depth of corrosion exceeded 75% of the wall thickness. Only moderate internal corrosion was found on any of the pipes and there were no examples of severe internal graphitic corrosion on

these pipe samples. This paper only considers graphitic corrosion that has occurred on the external surface of a trunk main.

A typical cross section of corroded cast iron pipe is shown in Figure 3. It is possible to identify three distinct areas of interest:

1. The fully transformed (“graphitised”) product of the graphitic corrosion process – “Region A”;
2. The original (uncorroded) cast iron – “Region B”; and
3. A “transition zone” that lies between the uncorroded and fully transformed material – “Region C”.

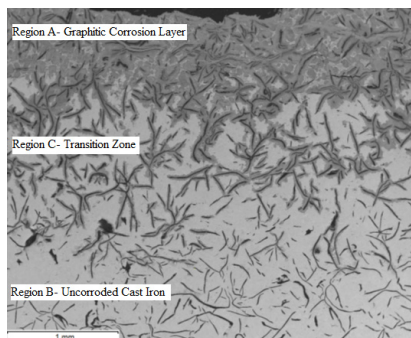


Figure 3: SEM image of cast iron cross section.

Region A: Grey cast iron consists predominantly of iron, with between 2.5 and 4% C, 1 and 3% Si, and typically < 1%P as well as other trace alloying elements. The carbon exists in the form of graphite flakes throughout the iron matrix [19]. It is the graphite content that gives grey cast iron its characteristic appearance of “scythe-shaped” graphite flakes within a matrix of ferrite and retained eutectoid.

Region B: Unlike other ferrous metals such as steels grey cast irons undergo a form of corrosion, known as graphitic corrosion that is unique to cast irons which leaves behind a porous residue consisting of graphite flakes interspersed with iron oxides and other insoluble products such as siliceous compounds and phosphide eutectic stringers [5].

Region C: The interface between regions A and B is not well defined but consists of a transition zone within which iron oxides are seen to be forming around the graphite flakes but much of the ferrite remains still in place.

It is an interesting observation that when a corroded cast iron sample is first sectioned and polished the presence of the transition zone is not obvious to the naked eye. Instead it appears that there is a single, distinct, interface between the original metal and the fully graphitised material (Figure 4). However, after 3 weeks exposure to air under ambient conditions an orange-coloured deposit forms on the surface of the cut metal in the region directly adjacent to the fully corroded layer (Figure 4). This surface deposit thickens and darkens with time, becoming a red/brown colour, whilst the bulk of the adjacent cast iron remains uncorroded. This region corresponds with the transition zone seen in Figure 3.

When polished this transition layer is easily removed, but returns after several days if left exposed to air, indicating that this interface region is hygroscopic and capable of supporting further corrosion reactions [11, 23].

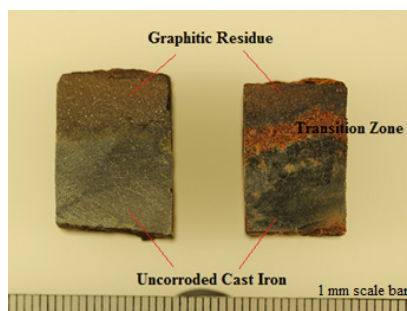


Figure 4: *Left:* freshly cut cast iron. *Right:* cast iron sample after 3 weeks in ambient conditions

The product of the graphitic corrosion process (within Region A of Figure 3) can be seen in greater detail in Figure 5(a).

It can be seen by comparison with the image of the uncorroded cast iron in Figure 5(b), that the original (ferritic) iron matrix has been replaced entirely with a compact iron oxide product, leaving behind a “skeleton” of graphite flakes and areas of uncorroded phosphide eutectoid stringers. Something clearly evident in this image that was not originally expected is that the graphite flakes have also deteriorated. The centre of the graphite flakes appear to be filled with the iron oxide corrosion product, giving them a “hollowed out” appearance. It also appears in this image that some graphite flakes have deteriorated. This is an interesting, and potentially important, observation. This suggests that the graphite flakes do not act exclusively as an inert cathode in the corrosion process but rather takes an active part in the deterioration mechanism.

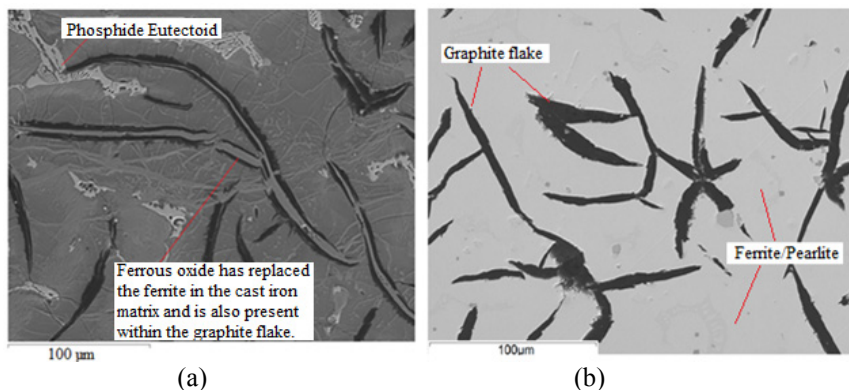


Figure 5: (a) SEM image of Region A. (b) SEM image of Region B.

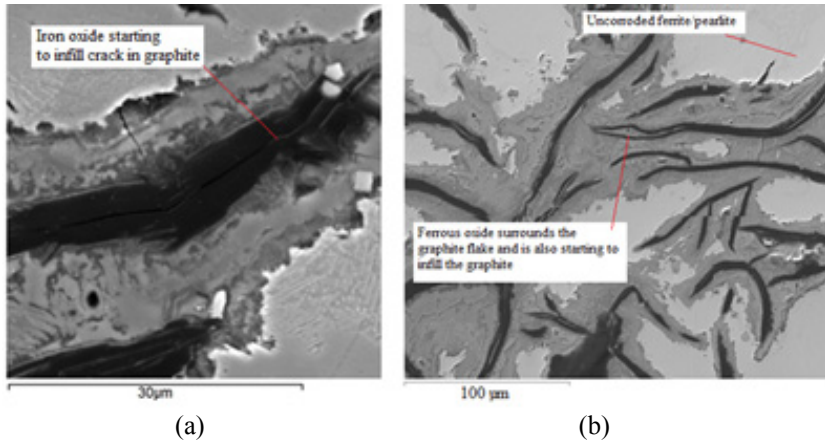


Figure 6: (a) SEM image of Region C. (b) Lower magnification of same area.

At even higher magnifications (Figure 6(a)), it is evident that during the corrosion process the graphite flake appears to be delaminating and undergoing significant changes in physical form. It is important to note that there are cracks within the graphite flakes which were not found in the bulk metal. Evidence that these cracks are not caused by the mounting process is shown by images of the iron oxide corrosion product in the process of filling these cracks.

Moving down into the transition zone, Region C, the graphite flakes are still in the process of delaminating/deteriorating (Figure 6(b)). One of the most interesting features has been found in the transition zone of four of the nine pipes examined. In the SEM image in Figure 7(a) there are bright features on the external surface of the iron oxide surrounding some of the graphite flakes.

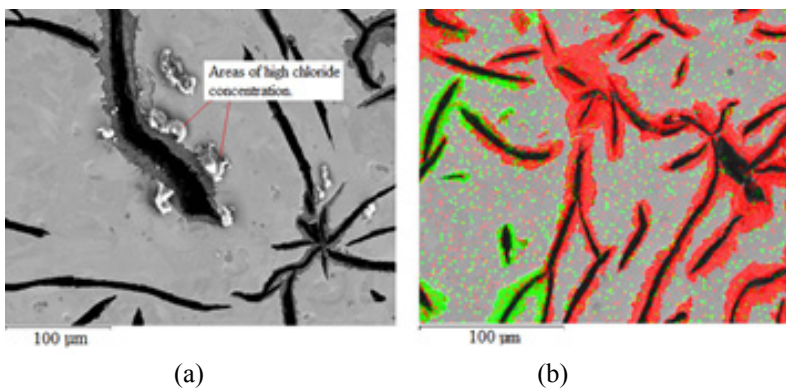


Figure 7: (a) SEM image of Region C. (b) Mixed EDX element map of Region C. Elemental chlorine surrounding the flake in the left side of the image is coloured green. Elemental oxygen is coloured red.

EDX spot analyses of these bright features reveal that these areas contain a high concentration of chloride ions, (between 5 and 11% by atomic weight). These features were only found in the transition zone of severely pitted cast iron. Element mapping by EDX of the cast iron samples also seems to confirm that these chloride concentrations are only found at the transition zone and not in the graphitic corrosion layer or the uncorroded bulk metal (Figure 7(b)).

Element mapping by EDX has shown chloride and silicon are present in high concentration within the oxide surrounding the graphite flake. The silicon concentration in the oxide material can be attributed to silicic acid that forms when the silicon originally present in the iron is oxidised. This suggests that the chloride ion plays a significant role in the corrosion process and is being concentrated at the leading edge of the transition at active anode sites. The ready (re)appearance of the transition zone in apparently “dry” samples left exposed to ordinary air post polishing is an observation also present in archaeological tests in relation to the protection of stored iron artefacts [11].

The SEM/EDX investigations in this study found that chlorides were a likely driver of corrosion in at least four of the nine pipes investigated. The link between chlorides and corrosion of cast iron is not new. Although the pipes were not in service in a marine environment there is still a likelihood of chloride build up in the soil over many years due to the run of from deicing salts [12, 18, 20]. Although there has been very little work by the water industry on the impact of chlorides in soil upon large cast iron structures, within the field of archaeology there is much interest in the effect of chlorides on the corrosion of buried iron artifacts [21–23]. Indeed, as many of the cast iron pipes still in use in the distribution network have been in the soil for over a century it is not unreasonable to view them as in-service antiquities.

A cast iron pipe that has been excavated after several decades in soil will typically be covered by a several layers of corrosion products. The outer layer will be a mixture of iron corrosion products, mainly goethite and other soil components such as clay, gravel and other minerals. Below this surface layer, are iron corrosion products in a lower oxidation state such as magnetite, goethite and green rusts. It is magnetite: a black coloured, electronically conducting, mixed Fe(II), Fe(III) compound, that is most likely to be the major corrosion product that has replaced the original ferrite and pearlite in the original cast iron [23, 24].

It is not inevitable that graphitic corrosion will continue throughout the thickness of a pipe wall, even after many decades underneath the ground. Although a graphitic corrosion layer does form on the buried pipe surface, the corrosion rate would appear to be minimal, with the graphitic corrosion layer acting as a coating, protecting the buried cast iron. However there are many cases where the corrosion has continued throughout the entire pipe wall thickness. The reasons for this are not fully understood, but one possible explanation could be the presence of chloride ions in the soil environment.

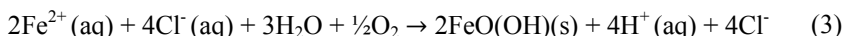
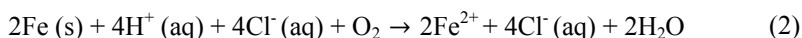
As long as the iron is corroding, Fe^{2+} ions are being formed at the interface between the bulk metal and the corrosion product. These Fe^{2+} ions will dissolve, accumulate and eventually hydrolyse to form precipitates. In order to maintain electrical neutrality, anions present in the soil environment, e.g. chlorides, will

diffuse into the corrosion product to balance the charge of the Fe^{2+} and H^+ ions. Chlorides in particular will accumulate at the corrosion interface. In acidic conditions the adsorption of chlorides at the interface is greater due to a net positive charge produced on the surface of iron oxyhydroxides by excess hydrogen ions. As the iron continues to corrode in the soil, the pores and cracks in the porous graphitic corrosion product will become filled with an acidic iron (II) chloride solution, with chloride ions concentrated at the corrosion interface [21].

It has been found that iron objects that have been contaminated with salts can experience accelerated corrosion after excavation from the ground. This has even been observed in iron objects that have been moved into a dessicated environment [25].

Moving the iron object to an environment with a lower relative humidity and higher oxygen content than when buried, results in a concentration of acidic FeCl_2 with the corrosion layers cracking giving the uncorroded surface of the metal more access to oxygen [23–26].

When an acidic solution of iron (II) chloride is exposed to air, hydrolysis of the iron ions can occur, oxidising the Fe^{2+} to Fe^{3+} , resulting in new compounds being precipitated as well as HCl . An acid regeneration cycle has been suggested for the corrosion of iron contaminated with chlorides [2].



The important step in the acid regeneration cycle is the formation of a soluble iron (II) salt from the chloride ions. It is the solubility of the salt that allows the process to continue. As the corrosion continues to occur, the iron is deposited within the corrosion layer, concentrating chloride ions at the surface of the bulk metal. Where chlorides are evenly dispersed throughout the corrosion layer, it is found that the corrosion rate is negligible [26, 27].

This correlates with the EDX mapping undertaken so far, as high concentrations of chloride have only been found in the graphitic pits. Sodium is not found in any great concentration within the transition zone or the fully corroded material, leading one to expect that it may have hydrolysed with water to form sodium hydroxide. This may provide an explanation for the deterioration of the graphite flakes. Graphite is known to be chemically inert against most acids at standard temperature, but will react with alkalis, notably sodium hydroxide.

5 Concluding remarks

The corrosion of cast iron trunk main is a significant issue for water utilities as it sits within a multi-cohort, multi-scale, multi-mechanism process for asset

management. The current work, which is part of a broader project to understand the behavior of deteriorated cast iron trunk main and the variables that lead to their present state, has examined the corrosion associated with nine pipes, taken from service. Previous work had noted that there was significant variation in the morphology of the corrosion present, and that it was possible for a single pipe to exhibit various conformations of corrosion product, as well as near as-cast condition material that was effectively uncorroded. (This was in marked contrast to small distribution main which tend to exhibit the same characteristics not only within the section of pipe examined but for significant lengths either side of the sampling position).

Here, small samples taken from these nine pipes have been examined using an SEM. Where corrosion has been observed, it has been found that at the transition zone at the bottom of corrosion pits ('icicles') significant concentrations of chloride ions are found to exist. These are not observed where the corrosion forms as 'icing'. A greater understanding of the graphitic corrosion process of cast iron trunk main in soils is needed to help predict corrosion rates of cast iron in soil, develop possible mitigation techniques to prevent further corrosion, and support the development of models to predict the lifetime of an in-service cast iron pipe or a network of such pipes [2].

Models used to predict the corrosivity of a soil environment will often take into account the soil resistivity, soil type, pH and moisture content. The work presented here shows that the presence of high levels of chlorides in the soil are also a major risk factor that need to be considered in any such models. High levels of chlorides may be found in marine/tidal soils and especially after road de-icing. There are numerous on-site techniques that can be employed to determine the chloride content of a soil. Should the chloride content in one area be shown to be high, further investigation may be necessary. Although the damage caused by soil chlorides on buried iron is well known within the field of archaeological preservation, few if any models used presently within the water industry to predict soil corrosivity, take soil chloride content into account.

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