Eng.&Tech.Vol.26,No.1,2008

Ductile and Gray Cast Irons Deterioration with Time in Various NaCl Salt Concentrations.

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Received on:12/12/2006

Accepted on 8/4/2007

Abstract

Gray cast iron is used in wide engineering applications especially pipes and these pipes are exposed to failure in most cases so that ductile cast iron is used instead of it later.

This project deals with the study of microstructure characteristics and chemical analysis for both materials in order to use them in the analysis of the microstructure after the corrosion tests involving immersion, polarization in different sodium chloride concentrations (0.01%, 0.58% and 3.5% NaCl).

Immersion results indicate that the corrosion resistance of both types of cast irons is excellent and ductile iron is better than gray cast iron and the reduction in corrosion rates for both materials is related to barrier layer deposited on the surface which is more uniform on ductile iron surface.

The electrochemical tests involve measurement of corrosion potential in open circuit using the same solutions for both materials and potentiostatic test is used to measure cathodic and anodic polarization in the above solutions. The test started from cathodic region to the anodic region with sweep rate of 10 mV/min to obtain the general behavior and measure the polarization parameters for both materials.

The measured corrosion potentials of the open circuit in all solutions are more noble values for gray iron than that for ductile iron. Corrosion potentials on polarization measurements point out to the same indication but the ability to start and form barrier layer in ductile is better than in gray iron.

Microstructure observations after the electrochemical tests indicate the presence of uniform layer on ductile surface and graphitization process is obtained on gray iron.

الخلاصة

يستخدم حديد الزهر الرمادي في تطبيقات هندسية واسعة أهمها الأنابيب ونتيجة لتعرض الأنابيب في معظم الأحيان للفشل لذلك استبدل بحديد الزهر ألمطيلي .

تضمن البحث دراسة خصائص البنية ألمجهريه والتحليل الكيمياوي لكلا النوعين لغرض استخدامها في تحليل نتائج البنية ألمجهريه بعد اختبارات التآكل بالغمر والاستقطاب لكلا المعدنين في تراكيز مختلفة من كلوريد الصوديوم (0.01 % ، 0.58 % و 3.5%) .

تشير نتائج الغمر بان مقاومة التآكل لكلا المعدنين ممتازة ومقاومة التآكل لحديد الزهر ألمطيلي أفضل من الحديد الرمادي والتناقص في معدل التآكل في كلا المعدنين مرتبط بالطبقة الحاجزة المترسبة والتي تكون أكثر تجانسا في الحديد ألمطيلي.

https://doi.org/10.30684/ etj.26.2.5

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ɔration with Time in Various NaCl Salt Concentrations.

الاختبارات الكهروكيمياوية تضمنت قياس جهد التآكل في الدائرة المفتوحة وبنفس المحاليل لكلا المعدنين واستخدام جهاز المجهاد الساكن لقياس الاستقطاب الكاثودي والانودي وبنفس المحاليل أعلاه حيث يتم الاختبار من المنطقة الكاثودية مرورا بجهد التآكل إلى المنطقة الانودية بمعدل استقطاب (10 m V/min) للحصول على السلوك العام وقياس معاملات الاستقطاب لكلا المعدنين .

جهود التآكل المقاسة باستخدام بالدائرة المفتوحة في جميع المحاليل لحديد الزهر الرمادي كانت قيمها أكثر نبلا من تلك المقاسة لحديد الزهر ألمطيلي. وتشير نتائج الاستقطاب إلى نفس النتيجة ولكن قابلية تكون الطبقة الحاجزة وبدئها أفضل في حديد الزهر ألمطيلي.

نتائج البنية ألمجهريه خلال التآكل اثبتت حصول طبقه حاجزة متجانسة على سطح **الحديد** ألمطيلي وحصول عملية الكر فتة بحديد الزهر الرمادي.

1. Introduction

The term “cast iron “designates an entire family of metals with a wide variety of properties. Cast irons are primarily iron with carbon as the main alloying element, which contains carbon in the range of 2-6.67 %C. Two percent is about the maximum carbon content at which iron can solidify as a single-phase alloy with all the carbon solution in austenite. Thus, the cast irons, by definition, solidify as heterogeneous alloys and always have more than one constituent in their microstructure. In addition to carbon, cast irons may also contain silicon or silicon is aded usually from 1 to 3 %; thus, they are actually iron-carbon –silicon alloys [1,2].

The predominant deterioration mechanism on the exterior of gray and ductile cast iron pipes are electrochemical corrosion with damage occurring in the form of pits. The damage to gray cast iron is often disguised by the presence of “graphitization”. Graphitization is a term used to describe the network of graphite flakes that remain behind after the iron in the pipe has been leached away by corrosion. Either form of metal loss represents a corrosion pit that will grow with time and eventually lead to a water main break. The physical environment of the pipe has a significant impact on the deterioration rate. Factors that accelerate corrosion of metallic pipes are stray electrical currents, soil characteristics such as moisture content, chemical and microbiological content, electrical resistivity, a reation, redox potential [3].

The interior of a metal pipe may be subjected to tuberculation, erosion, and crevice corrosion resulting in a reduced effective inside diameter. Severe internal corrosion may be also impact pipe structural deterioration. The supply water affects the internal corrosion in pipes through its chemical properties, e.g. pH, dissolved oxygen, free chlorine residual, alkalinity [4].

The shape of the graphite present in an alloy affects the mechanical properties of the material .Flake graphite acts as a severe stress while the spherodical graphite does not .A classic example of this effect is the difference between gray and ductile cast iron [5].

2. Experimental Work

The experimental work deals with specimens preparation, microstructure evaluation and corrosion rate measurements in different ways.

2.1 Materials

The materials used in this work were gray cast iron and ductile cast iron type. Chemical analysis of these materials was carried out using (Atomic absorption method) in Ibn-Sina Company.

2.2 Solutions

Solutions used in this work were 0.01%, 0.58% and 3.5% NaCl. These solutions were prepared by dissolving 0.1, 5.8 and 35 gm ANALAR sodium chloride in 1 liter of distilled water for each solution. After the solutions were prepared, pH of each solution was measured using pH- meter type (GT.BRITIAN) Philips.

2.3 Specimen Preparation

The specimens were cut out in dimensions of (2×2) cm and 0.5 cm thick for polarization test, and (5×2.5) cm and 0.3 cm thick for immersion test. The specimens were annealed at 560 C for two hours on derotor type furnace to release stresses. After cutting, specimens were abraded in sequence on 180, 220, 320, 500, 800, 1000 and 1200 grades of emery paper under running tap water on a hand grinder. Then specimens were polished and washed with tap water followed with distilled water and dried with a clean tissue, degreased by immersing them in acetone then dried with paper tissue and kept in a dissector over a silica gel bed.

2.4 Corrosion Tests

In this work, immersion studies, open circuit potential (OCP)-time measurements and potentiostatic polarization were used as the techniques for evaluating corrosion parameters of the (gray and ductile cast irons) in different sodium chloride concentrations.

2.4.1 Immersion Test

The prepared specimens were drilled near the upper edge and weighted before immersed in a 500-ml closed beaker in the above solutions of NaCl. The duration of exposure in solutions was: 24, 48, 96, 192, 384, 768, and 1532 hours. After different duration times, the specimens were chemicalg cleaned, dried, and weighted using digital balance type scaltec (0.0001) to obtain the weight loss before and after immersion to calculate the corrosion rate using equation (**MPY=534W/DAT**) [6].

2.4.2 Open Circuit Potential Test

The free corrosion potential for all different concentrations of NaCl was measured and determined by recording the potential of the specimen with respect to SCE with time for measuring using the digital multimeter. E_{corr} value was automatically recorded with variable value, until it reached a steady state value. The steady state value remained for 100 minutes so that we could consider the actual E_{corr} in this environment.

2.4.3 Potentiostatic Polarization Test

By using potentiostat (type PRT 10-0.5 L Nenking) polarization test was carried out. The potentiostat was connected to voltmeter and ammeter to read the applied voltage and current respectively.

The potentiostatic uses the constant potential while the change in current was read and recorded from the high resistance multimeter. The applied potentials were used for cathodic and anodic polarization for gray and ductile cast iron specimens. The potentials ranges are determined with help of corrosion potential obtained in open circuit test with sweep rate of 10mV/min.

3. Results and Discussions

3.1 Elemental Analysis

Table (1) shows the nominal and the analytical chemical compositions of two materials used in this work. This analysis indicate that the main elements of both cast irons are within the standard limits.

3.2 Microstructure Evolution

The microstructures obtained of two materials used are shown in Figure (1 a and b). The microstructure of gray cast iron appears in flake graphite form in matrix of ferrite and pearlite. The matrix also contains small amounts of graphite as shown in dark large areas shown in Figure (1 a). This microstructure description is also present in the international standard [9]. The measured hardness of gray cast iron is equal to (222HB), which is within the standard values of gray cast iron of (179-229) HB. The standard value of tensile strength of gray cast iron is of (173) Mpa. The microstructure of ductile cast iron consists of spheroidal graphite in matrix of full ferrite [Figure (1 b)]. The measured hardness of ductile type is equal to (186HB) and this value is within the standard limits of (143-187) HB. The standard tensile strength of this type of cast iron is (414) Mpa. The microstructures shown in Figure (1 a and b) are the typical microstructures of gray and ductile cast irons. The tensile strength values of spheroidal graphite irons are generally about twice those of flake graphite.

3.3 Corrosion Test

3.3.1 Immersion Test

The immersion tests were carried out on two types of materials (Gray and Ductile) in different sodium chloride solutions of 0.01%, 0.58% and 3.5% NaCl for different exposure times. The corrosion rates in these solutions were calculated using equation (MPY=534W/DAT), then corrosion rates versus time are plotted as shown in Fig.(2), (3) and (4) The corrosion rates in these Figures in the range of (1-5) mpy; this range is classified as excellent corrosion resistance ,which indicates high corrosion resistance for both types of cast irons. .

Fig. (2) illustrates that the corrosion rates of both cast irons are initially high and then decrease with time and steady state is established after 764 hours. The corrosion rate of ductile iron is lower than that for gray irons. Fig. (3) indicates relatively similar behavior except the steady state is established after exposure time of 388 hours. In 3.5% NaCl, similar behavior is observed as shown in Fig. (4). This behavior is independent of time after 380 hours exposure. The different exposure times for establishing the steady state corrosion rates in the above figures are inversely proportional to sodium chloride concentrations.

Fig. (5) indicates the effect of NaCl concentrations on corrosion rates of both types of cast irons for a fixed exposure time. The initial increase in corrosion rate is due to enhance solution conductivity. Higher dissolved salt decreases the solubility of dissolved oxygen, and corrosion rate steadily decreases beyond the maximum, at 3.5% NaCl. The corrosion rate of gray cast iron is higher than ductile cast iron in all salt concentrations. This also indicates higher corrosion resistance for ductile iron in all salt solutions.

The general behavior of cast iron in all figures is the same in which the corrosion rate is firstly high and then decreases as duration time increases due to the formation of barrier film with time and the metal dissolution rate decreases as shown in Fig. (6), (7) and (8). The barrier film on the surface is relatively regular in case of ductile cast iron and irregular in gray cast iron. This can be explained according to the microstructure characterization of gray with a flake graphite form which causes irregular barrier film formation, while the microstructure of ductile cast iron has a relatively uniform distributed nodular graphite form which induces more regular barrier film.

3.3.2 Electrochemical Measurements

3.3.2.1 Potential (OCP)-Time Measurement

The variations in the open circuit potential (OCP) of gray and ductile cast iron with time during their immersion in 0.01%, 0.58% and 3.5% NaCl solutions are shown in Figures (9) and (10) respectively. Figure (9) indicates the free corrosion potential of gray cast iron in different NaCl solution concentrations. All these curves are started at a relatively same potential and slightly decrease the potential to more negative value. Steady state potentials are established for all curves. Noting that the decrease in potential is related to NaCl solution concentrations; higher decrease is relatively present at 3.5%NaCl solution and so on.

Fig. (10) shows the free corrosion potential of ductile iron in different NaCl solution concentrations. The potential-time behavior is similar to that of gray cast iron, and the potentials for 0.58% and 3.5% NaCl solutions are relatively very close to each other. The potentials are also related to NaCl solution concentrations.

In general, the potentials for both types of cast irons are changed from an initial high negative value to a more negative value within about 30 minutes and then the potential remains stable at this value. The values of free corrosion potential for both cast irons in different concentrations are shown in Table (2).

3.3.2.2 Potentiostatic Polarization Measurements

The polarization tests were carried out by using potentiostatic equipment on two types of materials (Gray and Ductile) in different sodium chloride solutions of 0.01%, 0.58% and 3.5% NaCl. The electrochemical behaviors of two types of cast irons were studied in these concentrations. Test specimens were polarized from cathodic to anodic regions at sweep rate of 10 mV/min. The potential log current density plots obtained for polarization different specimens of both type of cast irons in these solutions are shown in Fig. (11), (12) and (13).

Fig. (11) shows cathodic and anodic polarization curves of both types of cast irons 0.1wt% NaCl solution. It indicates that corrosion potential has less negative value than for ductile cast iron, this means that the corrosion potential of gray iron is more noble than of ductile. Therefore the anodic dissolution current of ductile cast iron is firstly larger than that for gray iron corresponding to the active dissolution zones, but the barrier film formation on the ductile cast iron is started before the barrier film formation on the gray cast iron due to regular form and distribution of graphite phase in ductile and irregular forms and random distribution in gray cast iron. The barrier potential of ductile cast iron is lower than that for gray iron as shown in Tables (3) and (4). The pitting formation for both cast irons is likely to be repassivated as shown in point A. The slight increase in current density in the barrier region may be due to dissolution around the graphite phases. These phases are removed from the surface due to galvanic action. These regions are likely to be pitting formation as shown in Figure

(15a). This dissolution can be indicated by the sudden increase in points A and B (Fig. 11).

Fig. (12) indicates the corrosion behavior curves of both types of cast irons in 0.58wt% NaCl solution. The behavior is similar to that shown in Fig. (11) except the differences in the corrosion potential and other parameters. Fig. (13) illustrates the cathodic and anodic behavior of both types of cast irons in 3.5wt% NaCl solution. This figure shows a similar behavior to those behaviors on 0.1 and 0.58 wt% NaCl solutions.

Generally, the corrosion behavior for both types of cast irons in different sodium chloride solutions indicates that the corrosion potential for gray iron is more noble than that for ductile iron but the ability of ductile iron to form barrier film is higher than that for gray iron in most cases. The different parameters of polarization curves of gray and ductile cast irons are shown in Tables (3) and (4) respectively.

The corrosion rates of gray and ductile cast irons in different salt solutions are shown in Figure (14). Higher corrosion rates are related to cast iron types and higher concentration of sodium chloride solutions. Higher concentration of NaCl solution produces higher conductivity which enhances the absorption of chloride ions on the cast iron surfaces and then increases the dissolution rate of metal.

Microstructure observation on polarization specimens of both types of cast irons are shown in Fig. (15) and (16). Fig.(15) indicates the

the cast iron surfaces and then increases the dissolution rate of metal.

Microstructure observation on polarization specimens of both types of cast irons are shown in Fig. (15) and (16). Fig.(15) indicates the microstructure of gray polarized specimens showing large white areas as graphitization effects and dark areas as pits formation. The graphitization effects in this case is greater than pits formation. Graphitic corrosion occurs exclusively in gray cast iron, which has a continuous graphite network in its microstructure. The graphite, acting as cathode, accelerates anodic dissolution of nearby iron, leaving behind the graphite network, which maintains structural shape but loses mechanical strength. Ductile or malleable cast irons do not have a continuous graphite network. Although they corrode by uniform penetration, graphitic corrosion is not present. Fig.

microstructure of gray polarized specimens showing large white areas as graphitization effects and dark areas as pits formation. The graphitization effects in this case is greater than pits formation. Graphitic corrosion occurs exclusively in gray cast iron, which has a continuous graphite network in its microstructure. The graphite, acting as cathode, accelerates anodic dissolution of nearby iron, leaving behind the graphite network, which maintains structural shape but loses mechanical strength. Ductile or malleable cast irons do not have a continuous graphite network. Although they corrode by uniform penetration, graphitic corrosion is not present. Fig. (16) shows the microstructure of ductile polarized specimens which illustrates that the pit formation areas are greater than graphitization areas.

4. Conclusions

From the results obtained in the present work, the following conclusions can be drawn:

1. The corrosion resistance of ductile iron is better than that of gray iron in different concentrations of NaCl solutions which is related to form and uniform distribution of graphite phase on ductile iron.
2. Corrosion potential for gray iron is more noble than for ductile iron.
3. The ability to form barrier film on ductile iron is better than for gray.
4. Graphitization appears more clear on gray iron than on ductile iron.
5. The above conclusion indicates that ductile iron has better properties to use it in pipe applications.

(16) shows the microstructure of ductile polarized specimens which illustrates that the pit formation areas are greater than graphitization areas.

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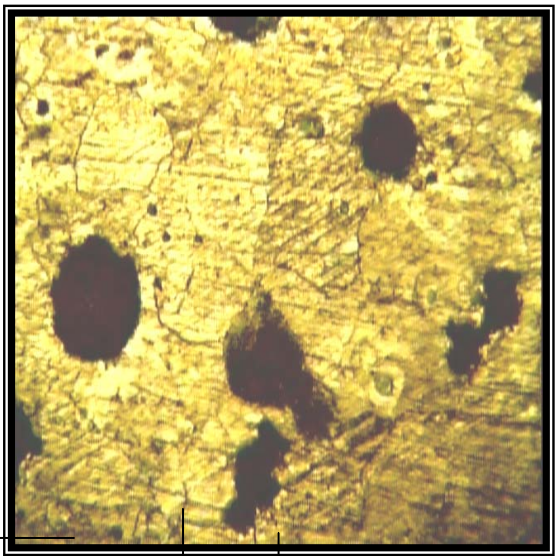
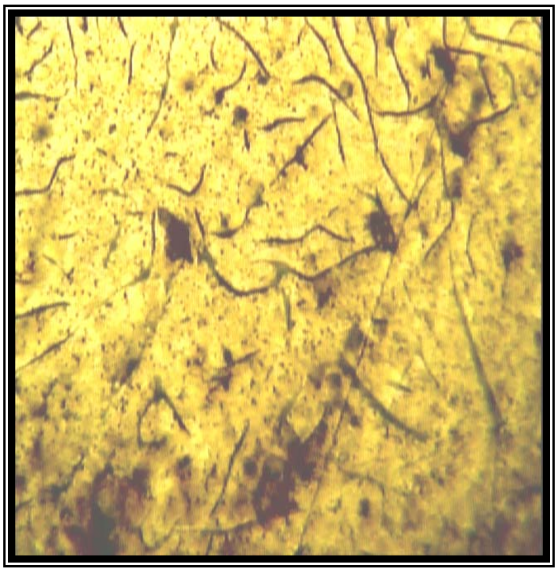
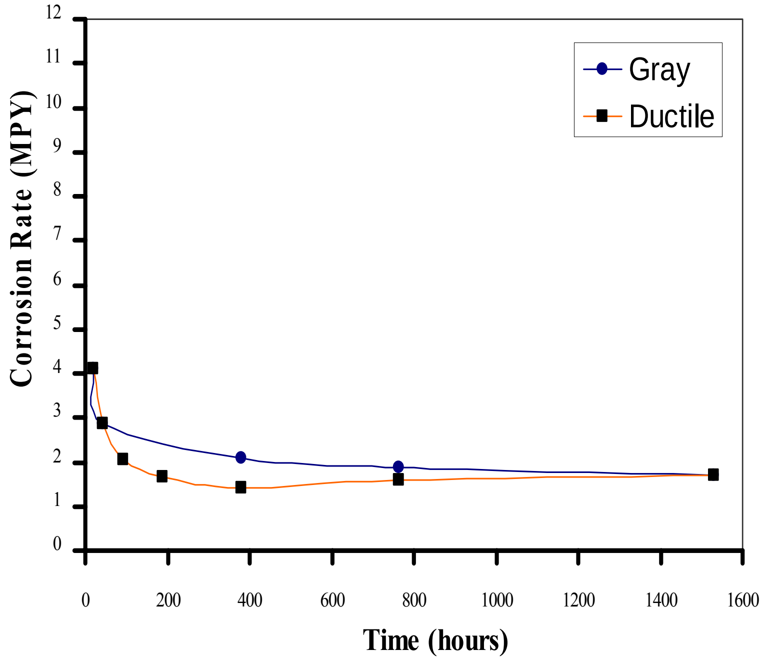
Table (1) A nominal [7, 8] and analytical chemical compositions of gray and ductile cast irons.

Chemical composition	Gray		Ductile	
	ASTM	Analytical	ASTM	Analytical
C%	3.2-3.5	3.5	3(min)	3.1
Si%	2-2.4	2.02	2.5(max)	1.68
Cr%	0.05-0.20	0.053	0.8(max)	0.25
Mo%	0.05-0.10	0.0098	0.01-0.10	0.017
Ni%	0.05-0.20	0.054	0.05-0.20	0.085
Mn%	0.6-0.9	0.62	0.30-1.0	0.45
Cu%	0.15-0.40	0..16	0.15-0.4	0.2
P(ppm)	0.20	<0.25	0.08(max)	<0.25
Mg%	---------	---------	0.03-0.05	0.04
C.E	4.0-4.25	4.16	-------	------







Figure(2)Corrosion rate of gray and ductile in (0.01% NaCl).

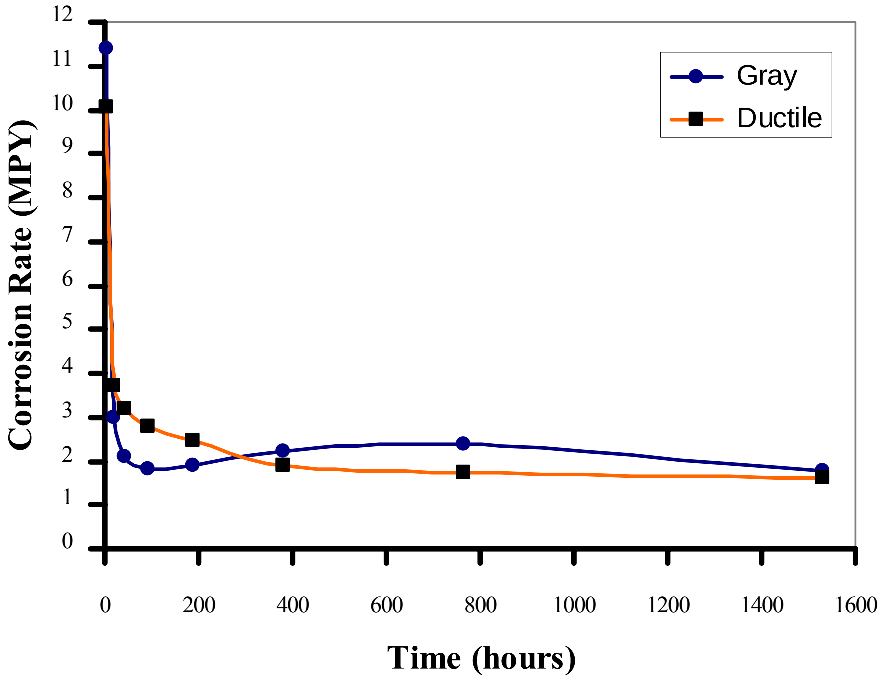


Figure (3) Corrosion rate of gray and ductile(0.58% NaCl).

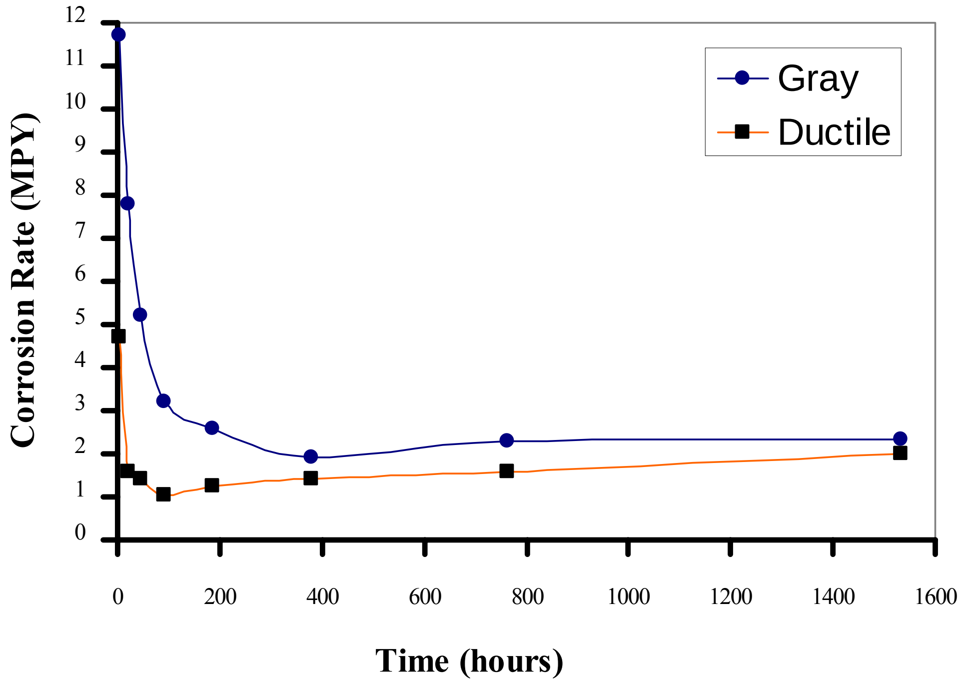


Figure (4) Corrosion rate of gray and ductile in (3.5% NaCl).

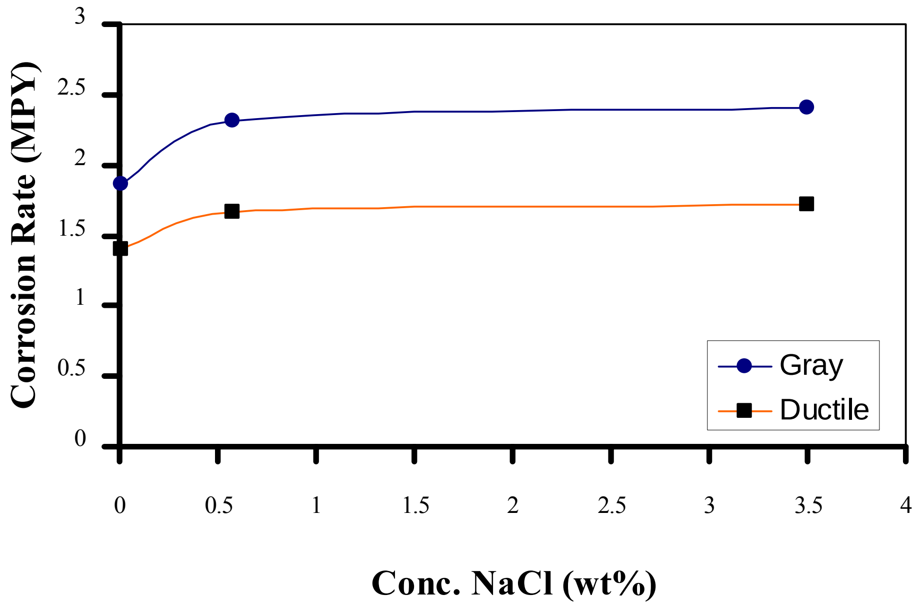
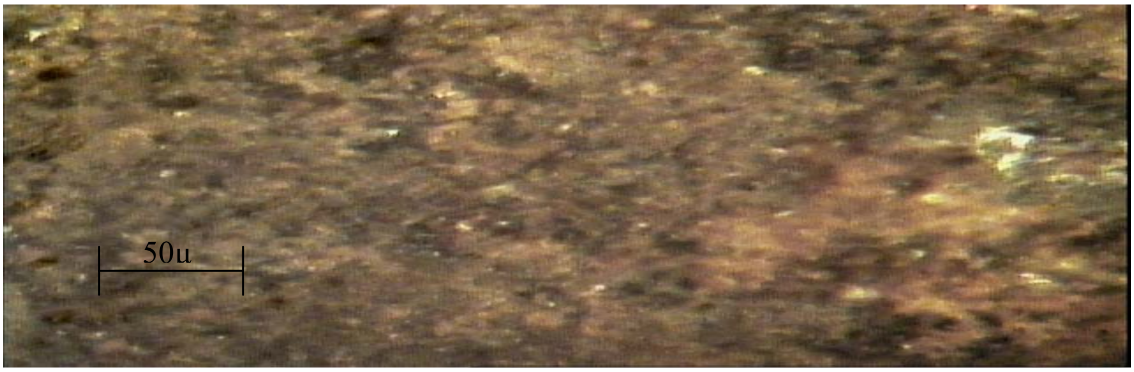


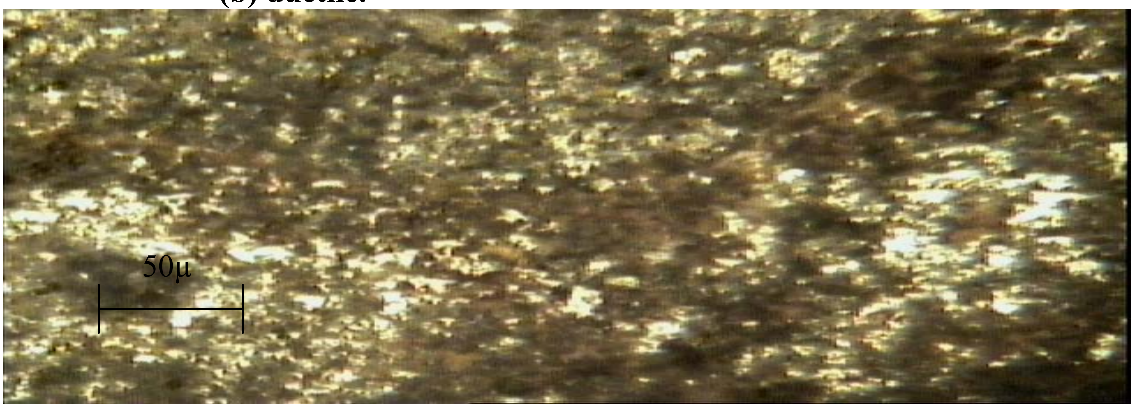
Figure (5) Effect of NaCl concentrations on corrosion rate of gray and ductile cast irons at (Time=764 hs).

(a)



(b)

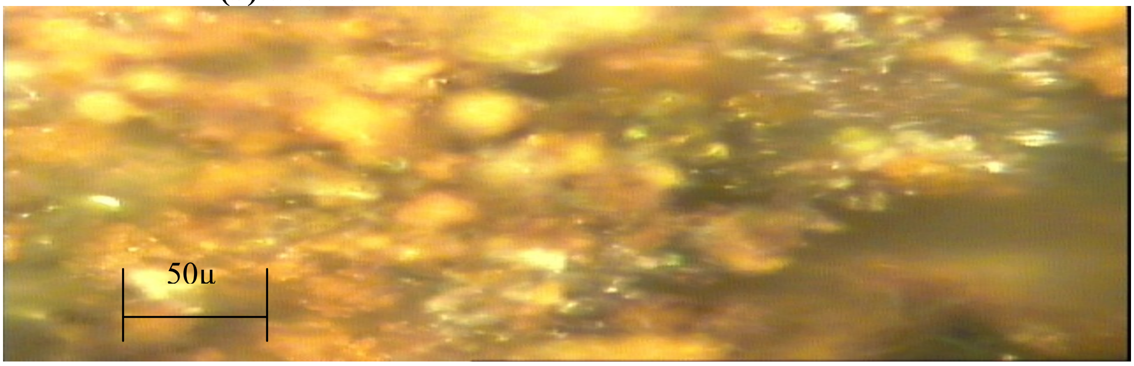
Figure (6) The barrier film formation on the materials after the immersion in 0.01%NaCl (a) gray (b) ductile.



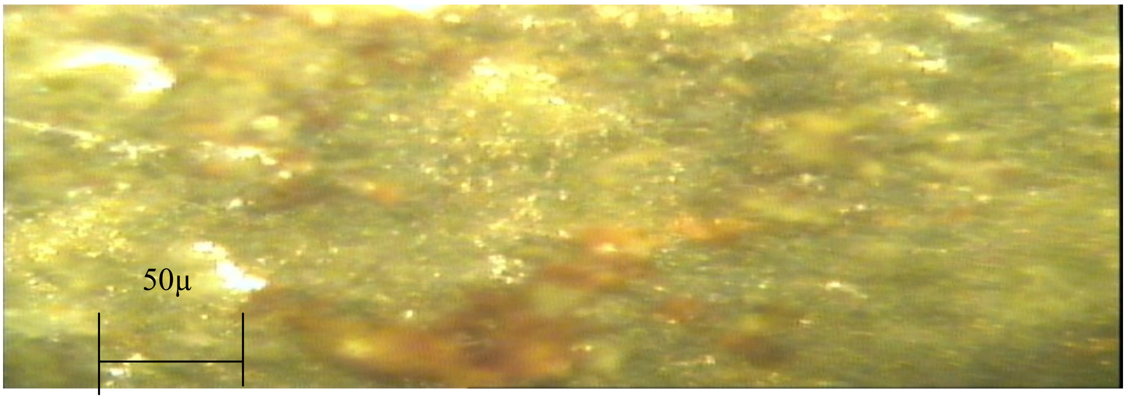
(a)

(b)

Figure (7) The film barrier formation on the materials after the immersion in 0.58%NaCl (a) gray (b) ductile.



(a)



(b)

Figure (8) The film barrier formation on the materials after the immersion in 3.5%NaCl (a) gray (b) ductile.

Table (2) Corrosion potential of gray and ductile cast irons vs. SCE.

Concentrations of NaCl%	**Free corrosion mV (gray)**	**Free corrosion mV (ductile)**
0.01	-716	-743
0.58	-717	-766
3.5	-747	-767

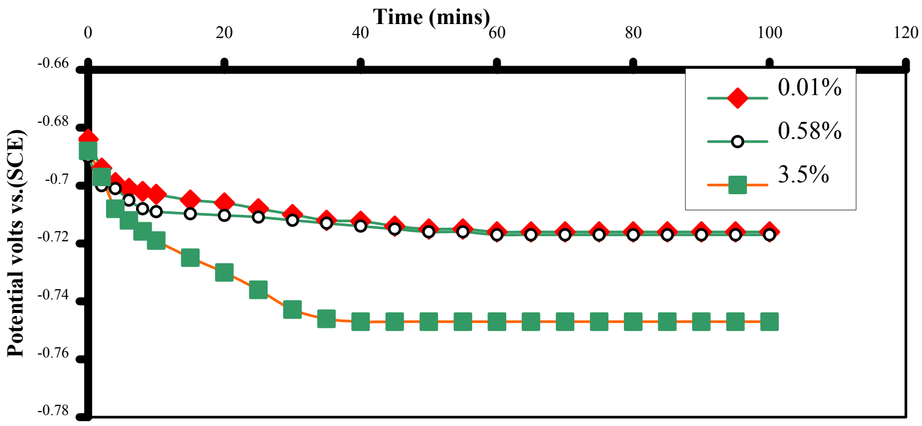


Figure (9) Corrosion potential of gray cast iron in different salt solutions.

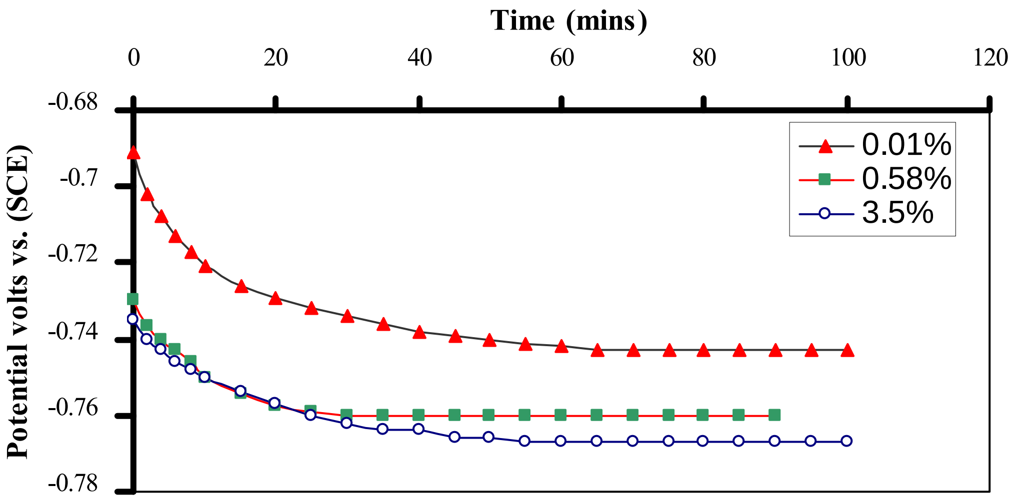


Figure (10) Corrosion potential of ductile cast iron in different salt solutions.

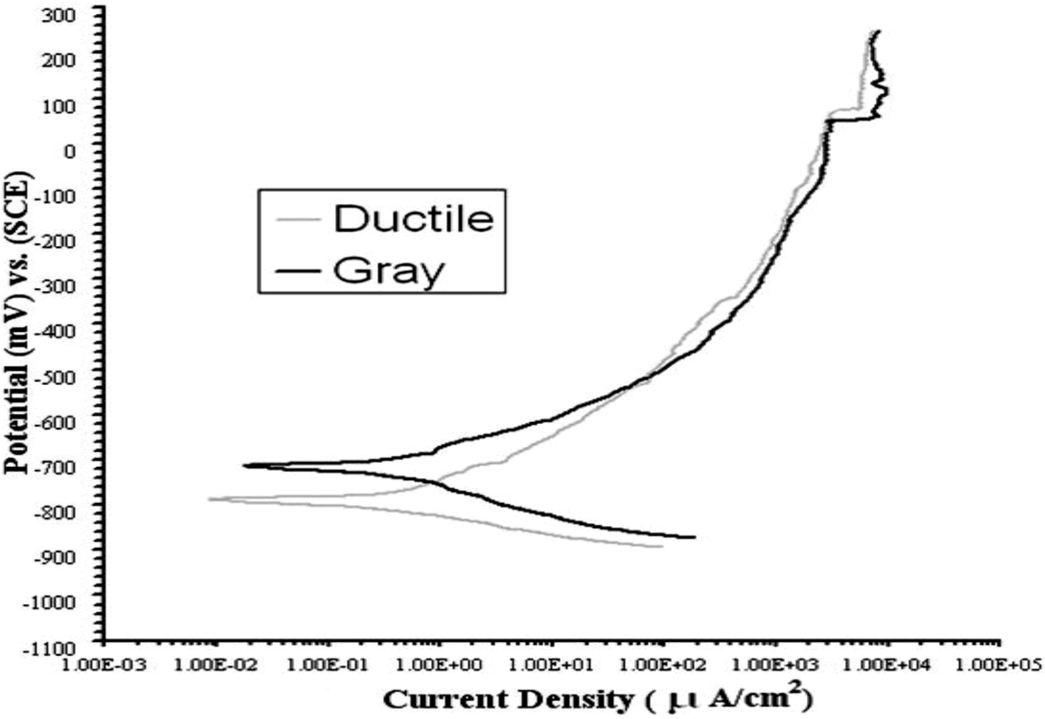


Figure (11) Polarization curves of gray and ductile irons in 0.01% NaCl.

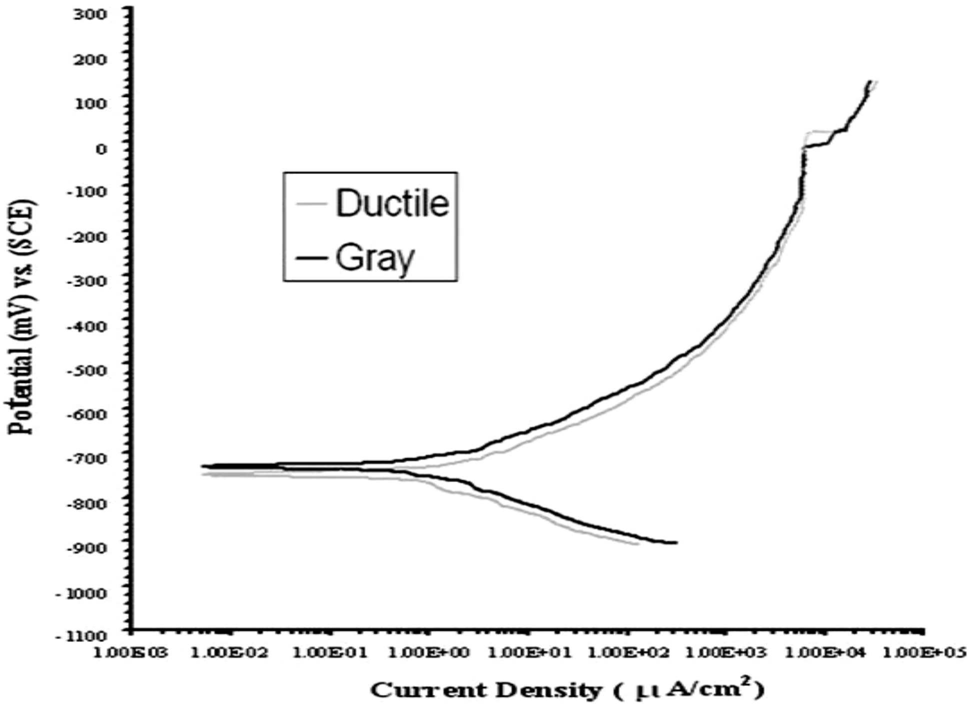


Figure (12) Polarization curves of gray and ductile irons in 0.58% NaCl.

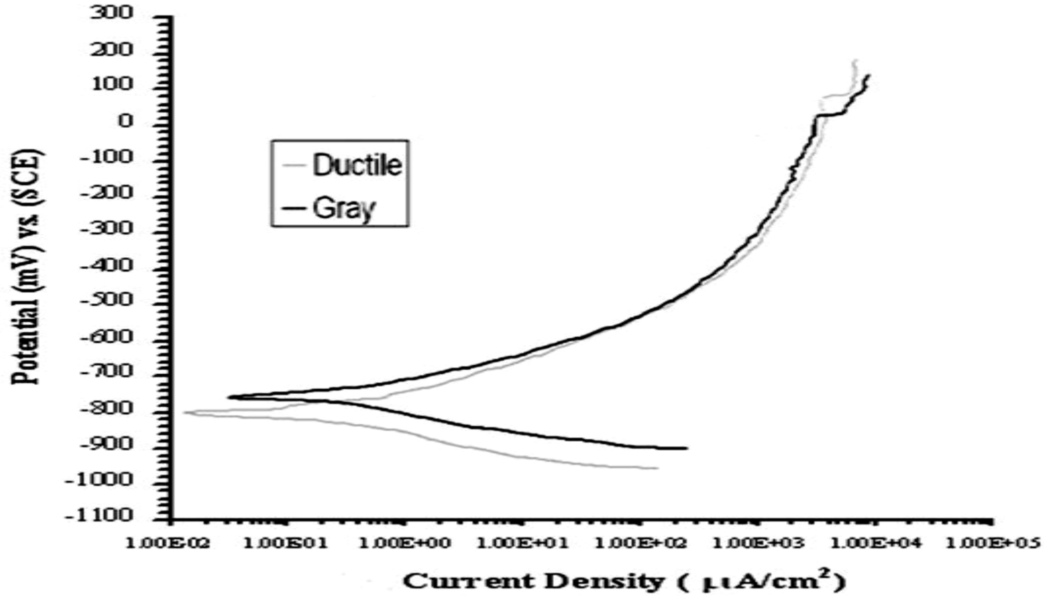


Figure (13) Polarization curves of gray and ductile irons in 3.5 % NaCl.

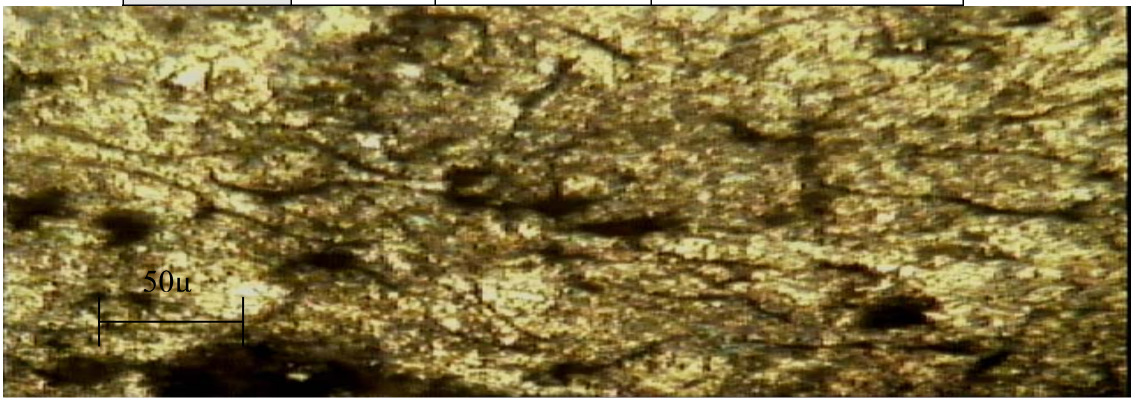
Figure(14)The effect of variation in sodium chloride concentrations on corrosion rate of gray and uctile cast irons.

Table (3) Polarization parameters of gray cast iron.

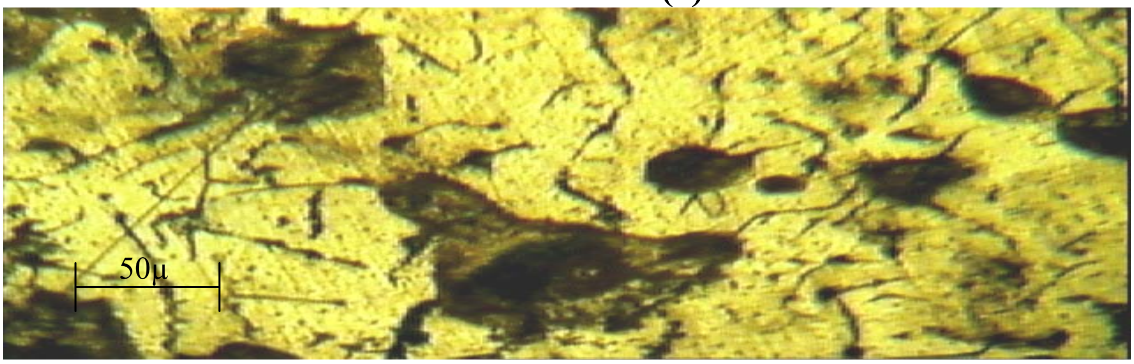
Conc.%	E_{corr} **mV**	**i_{corr} μA/cm^2**	C.R(MPY)
0.01	-699	$9x10^{-1}$	1.3
0.58	-722	0.95	1.4
3.5	-753	$8x10^{-1}$	1.5

Table (4) Polarization parameters of ductile cast iron.

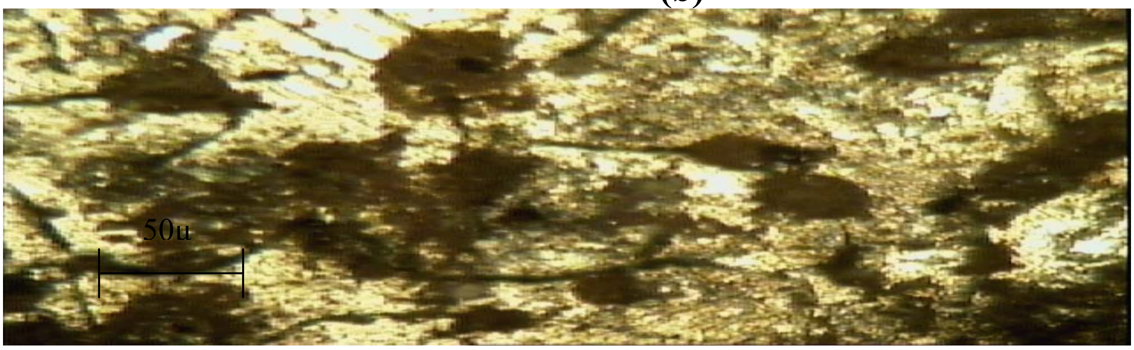
Conc.%	E_{corr} mV	i_{corr} $\mu A/cm^2$	C.R(MPY)
0.01	-735	$1x10^{-1}$	0.13
0.58	-755	$3x10^{-1}$	0.41
3.5	-780	$9x10^{-1}$	1.2



(a)

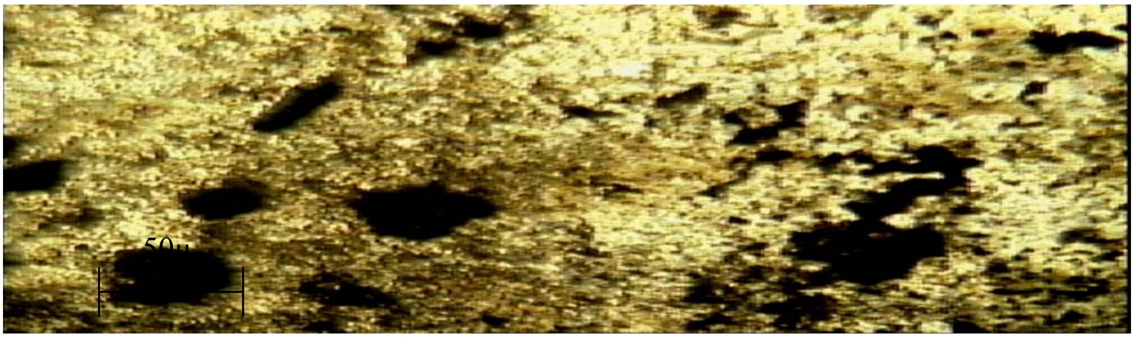


(b)

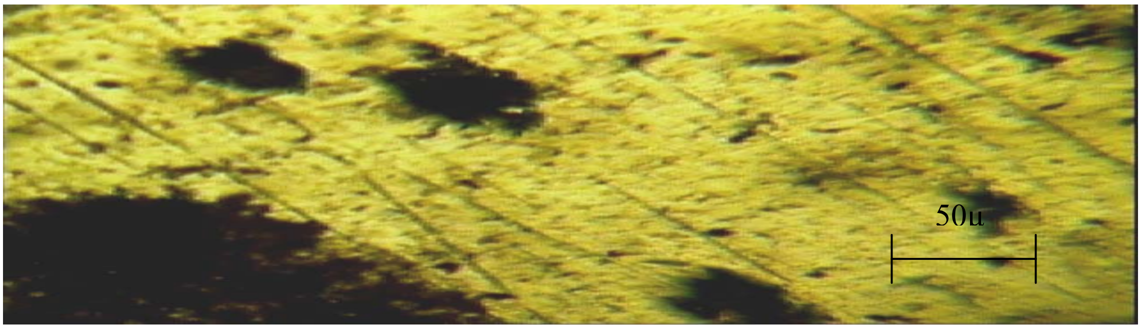


(c)

Figure (15) The gray cast iron showing pitting corrosion in (a) 0.01%, (b) 0.58% and (c) 3.5% NaCl



(a)



(b)

(c)

Figure (16) The ductile cast iron showing pitting corrosion in (a) 0.01%, (b) 0.58% and (c) 3.5% NaCl.