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Full Length Research Paper

Environmental surface degradation of galvanised and mild steels in cattle and poultry wastes and urea solution

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An investigation of the corrosive properties of cattle and poultry dung/urine slurries and urea solution and by extension, the corrosion resistance of galvanised and mild steels in these respective test media was performed by the weight loss method. The results showed corrosive surface degradation of galvanised steel and extensive corrosion of the mild steel test specimens by the corrosive constituents of the various test media. The corrosive constituents in the slurries are believed to be urea, uric acid, ammonia and ammonium salts, naturally excreted chloride (common salt), carbon-dioxide and sulphate reducing and sulphur oxidizing bacteria. The galvanised steel is found to be more corrosion resistant than the mild steel. The cattle dung/urine slurry was found to be the most aggressive of the test media and the poultry dung/urine slurry, the least corrosive medium.

Key words: Corrosion, galvanised and mild steels, surface degradation, slurries, agriculture, urea solution, environment.

INTRODUCTION

Agriculture represents one of the largest sectors of our national industry in which at least about 70 to 80% of the population are involved; though this industry is still more in the hands of peasant farmers. The trend of large scale farming, particularly, animal husbandry by corporate bodies, Governments, industrialists, and individuals; and the general interest in Agro-allied industries by these concerns, has made the agriculture industry to be capital intensive. This involves investments per acre varying widely, depending upon the particular activity. High investments are found where structures are involved.

Corrosion losses in agriculture in the country have not been quantitatively determined, just as in any other industrial sectors. It is believed, however, that first-order costs which take into account material losses and labour will be enormous. Second-order losses arising as a consequence of corrosion which includes loss of crops due to breakdown of machines and straying of animals through failed fences (Guide to practice) could multiply the first-order costs three times.

Corrosion costs in Nigeria, in particular, is assumed or anticipated to be high. By better application of existing knowledge in corrosion and protection and in materials selection, about one third could be saved (Guide to practice). Though, there is no known study which estimates what proportion of corrosion losses in agriculture could be saved, studies abroad suggested it could be as much as 50% (Fowler et al., 1081). With a huge investment in agriculture in the country and annual corrosion losses which is expected to be substantial, one half of which could be saved, a better appreciation of corrosion and what can be done to prevent it is clearly worthwhile.

The wide variety of structures, machinery and fittings employed for farming purposes makes it difficult to define precisely and concisely where corrosion can be most damaging. The situation is further complicated by the different types of environment (rural, urban, coastal), the local ‘microclimate’ the type of farming activity, the seasonal use of certain equipment and machinery and the

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methods employed for storage.

The intensification of animal husbandry has increased the problems of handling manure, and much equipment has been developed to cope with large quantities involved. Slurry is a mixture of dung and urine: and farmyard manure (FYM) is slurry composited with litter that is, straw or wood shavings, etc. Both ferment to release moisture, NH_3 and CO_2 (Agriculture Department Advisory Service). The major chemical constituents in slurry and FYM, have been determined to be urea, uric acid, ammonia and ammonium salts and naturally excreted chloride (common salt). The mixture could be corrosive towards steel structures and machinery that are poorly protected and maintained. Further use of fertilizers in agriculture also means increase in corrosion by agricultural chemicals. The main chemicals of the liquid fertiliser – nitrogenous solutions are ammonium nitrate and urea. The intense slurry action in the poultry and cattle houses could cause severe corrosion attack (Courshee, 1956; Eker and Yuksel, 2005; Scouten and Gellings, 1987; Rother, 1980; Severnyi et al., 1985) due to the internal atmosphere that could contain ammonia in high concentration. Similar attack could also occur where manure and fertilisers are used.

Mild steel is used in this work because it is the most abundant and most commonly used metallic material in agriculture. Galvanising of steel is generally beneficial in resisting corrosion and this accounts for the selection of galvanised steel in this investigation. Urea is used not only to simulate its corrosion characteristics as a constituent of slurries, but also as the second major constituent of nitrogenous solutions – liquid fertiliser used in agriculture.

The object of this investigation, therefore, is to evaluate the corrosion behaviour of mild and galvanised steels for proper material selection in agriculture, and animal husbandry handling activities, in particular. This is of considerable economic importance.

EXPERIMENTAL PROCEDURE

Materials

Two different types of metallic materials were used for the experiments. These are:

i. Flat sheet galvanised steel obtained from the Galvanising Industry, Lagos.
ii. Hot rolled cylindrical mild steel of 7.5 mm diameter obtained from the Oshogbo Rolling Mill Co. Ltd., Nigeria. Its average chemical composition was: 0.15% C, 0.23% Si, 0.5% Mn, 0.04% P, 0.025% Cu, 0.04% S, 0.10% Cr, 0.11% Ni, 0.05% Sn and the rest Fe.

Preparation of test specimens

The galvanised steel sample was cut into several rectangular plates, each of 20 x 20 x 0.9 mm. Similarly, the cylindrical mild steel was cut into several pieces. Each test specimen was 20 mm long.

The mild steel's cylindrical surface was scraped with a scraper all over and the two surfaces of the diameter were ground with silicon carbide abrasive papers of gifts 240, 320, 400 and 600. The galvanised steel and the mild steel were then thoroughly rinsed with distilled water, cleaned in acetone and stored in a desiccator for further tests. The edges of the galvanised test specimens which had no zinc coating due to cutting, were lacquered to concentrate attention on the zinc coated flat surfaces. One of the mild steel test specimens was further polished to 0.1 mm and etched in 2% Nital etchant for the surface metallographic examination.

Preparation of test media

The test media consisted of:

i. Cattle dung/urine slurry
ii. Poultry dung/urine slurry, and
iii. Urea solution.

The cattle and poultry dung were collected from the Teaching and Research Farm of the Obafemi Awolowo University, Ile-Ife. The urea crystal was of the AnalaR grade. The cattle and poultry dung excreted on the day of commencement of the experiment were collected. 1 kg of each of the cattle and poultry dung was mixed with 1 L of distilled water in two separate beakers. Each of the slurries was later divided into two equal portions, to make up four beakers of slurries. Urea solution of 0.5 M was also prepared using distilled water.

Weight loss experiments

Weighed test pieces of mild steel and galvanised steel were separately immersed in each of the cattle and poultry slurries and in the urea solution contained in beakers for a period of 30 days. The test specimens were taken out every three days, washed with distilled water, rinsed with acetone, dried and reweighed. All the experiments were performed at ambient temperature. Plots of weight loss versus time of exposure were made (Figures 1 and 3). Curves for corrosion rate (calculated) versus time of immersion were also plotted (Figures 2 and 4).

Metallographic examination and photomicrographs

Metallographic examination of the prepared and etched surface of the mild steel was performed using a metallurgical microscope. Photomicrographs were made of the mild steel surface and also of the clean surface of the galvanised steel test specimen. At the end of the experiment, the test specimens were again examined under the microscope and photomicrographs of representative areas were made (Figures 5 and 6).

EXPERIMENTAL RESULTS

Galvanised steel test specimens

The curves of weight loss (g/mm^2) versus the exposure time (days) for the galvanised steel test specimens immersed, in turns, in cattle and poultry dung/urine slurries and in urea solution, respectively, are presented in Figure 1. In all the test media, there was increase in weight loss of the specimen with exposure time. However, the cattle dung/urine slurry has the highest amount of weight loss throughout the experimental period. The weight loss was drastic in the first six days of

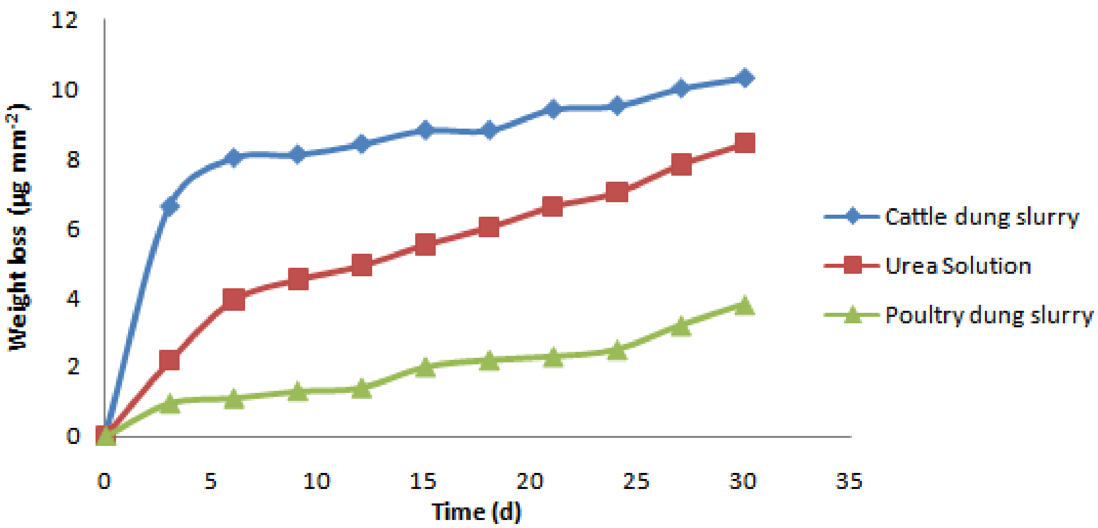


Figure 1. Variation of weight loss with time for the galvanised steel test specimens immersed in cattle.

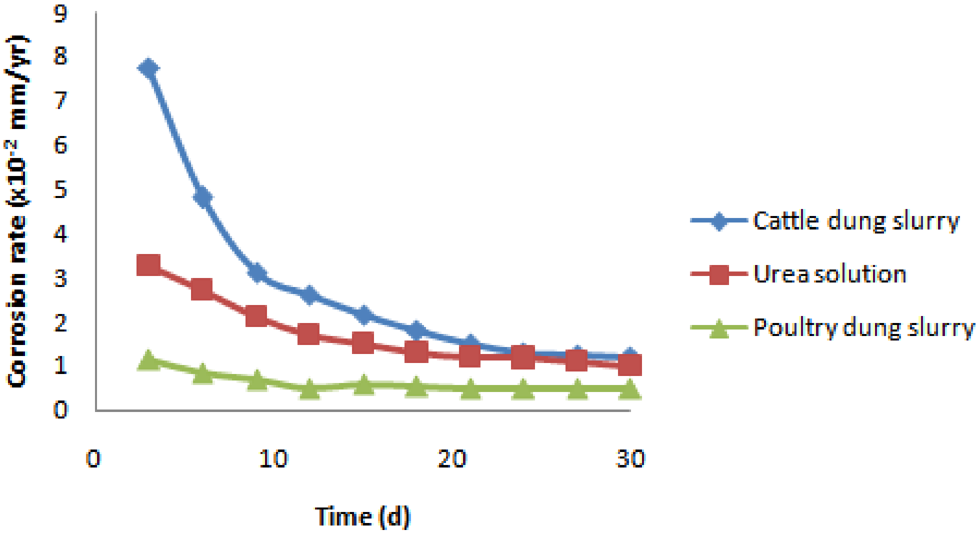


Figure 2. Variation of corrosion rate with time for the galvanised steel specimens immersed in cattle and poultry dung/ urine slurries and in urea solution.

the experiment. Increase in weight loss after this period remained very gradual to the 30th day of the experiment. The curve obtained for the specimen's weight loss in urea solution shows that this medium was corrosive and it was next in corrosion magnitude to the cattle dung/urine slurry. The curve of the weight loss versus the exposure time shows an almost linear relationship. Comparatively, the curve obtained fir the poultry dung/urine slurry indicates the smallest amount of weight loss of the test specimen.

Figure 2 shows the curves of variation of corrosion rate (mm/yr) with the exposure time for the galvanised steel immersed, in turns, in the cattle and poultry dung/urine slurries and in urea solution. Corrosion rate in cattle dung/urine slurry, as shown in the curve, decreased very steadily with the increasing time of the specimen's immersion in the test medium, till the end of the experiment on the 30th day. The decrease in corrosion rate in the first 12 days of the experiment was drastic. This curve shows the highest amount of corrosion rate for 27 days of the experiment.

Corrosion rate in urea, Figure 2, decreased with time throughout the experimental period but this was very gradual and almost reaching a steady state relationship with exposure time from the 18th day of the experiment to the 30th day – the end of the experiment. The rate of

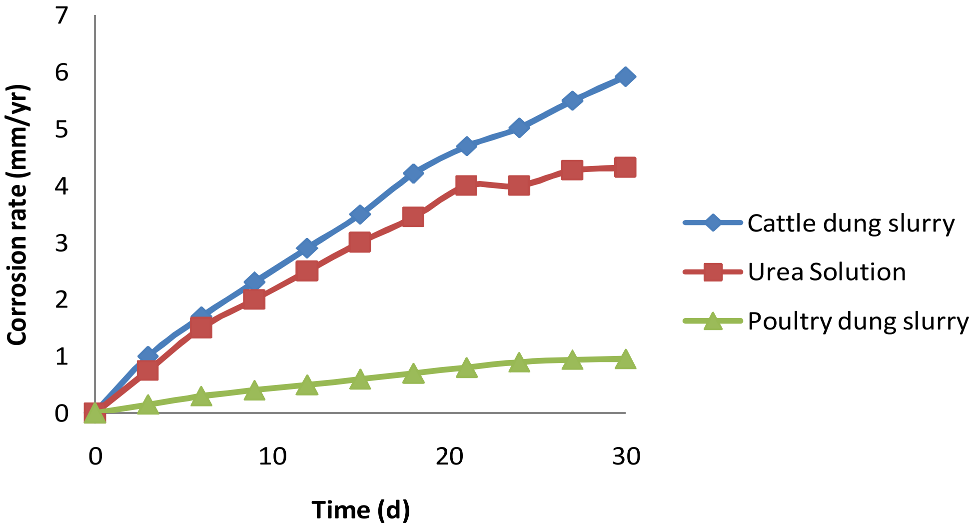


Figure 3. Variation of weight loss with time for the mild steel test specimens immersed in cattle and poultry dung/urine slurries and in urea solution.

corrosion here was comparatively less than that of the cattle dung/urine slurry.

The poultry dung/urine slurry gave the lowest corrosion rate for galvanised steel throughout the experimental period (Figure 2). The corrosion rate of galvanised steel in this medium was gradual to about the 12th day of the experiment; when it increased slightly to the 15th day. After the 15th day of the experiment, the corrosion rate remained in an almost steady state relationship with exposure time till the end of the experiment on the 30th day.

Mild steel test specimens

Figure 3 shows the curves of the weight loss versus the exposure time for the mild steel test specimens immersed, in turns, in cattle and poultry dung/urine slurries and in urea solution, respectively.

Corrosion of the test specimen in the cattle dung/urine slurry was most severe comparatively. This was indicated by the highest amounts of metal weight loss throughout the most part of the experimental period (30 days), though the curve shows some scattered points. Urea solution was also corrosive to the mild steel. The weight loss of the test specimen in this medium, increased with time of exposure throughout the period of the experiment. The weight loss of the mild steel specimen in this test was not as much as in the cattle dung/urine slurry, though very near that. Weight loss of mild steel in the poultry dung/urine slurry increased very gradually and slowly with exposure time. The weight loss was small throughout the thirty days of the experiment. The maximum amount of weight loss was 0.75 x 10^{-4} g mm^{-2} on the 30th day. It was the least corrosive medium used.

The curves of corrosion rate (mm/yr) versus the exposure time (days) for the mild steel test specimens immersed, in turns, in the above mentioned test media are presented in Figure 4. Corrosion rate for the test specimen in the cattle dung / urine slurry decreased with exposure time drastically in the first 12 days of the experiment, increased to the 15th day and then decreased to the 24th day of the experiment. There was also an increase in corrosion rate between the 24th and the 27th day of the experiment before the final decrease to the end of the experiment on the 30th day. Corrosion rate of the mild steel test specimen in urea solution decreased with exposure time though gradually, throughout the experimental period. The corrosion rate was high like in the cattle dung/urine slurry. Though, slightly lower than the former, the poultry dung/urine slurry gave the lowest corrosion rate throughout the experimental period. The corrosion rate decreased very gradually with exposure time till the 30th day of the experiment.

Comparison of the corrosion resistance of the test specimen in the test media

Table 1 and the various curves made as mentioned above show that the corrosion resistance of galvanised steel specimen in the different test media is better than that of the mild steel photomicrograph made from the metallurgical microscope examination of the galvanised steel test specimens surface before and after immersion in the different test media are presented in Figure 5(i-iv). Similar photomicrograph results for the mild steel specimen before immersion in the test media are presented in Figure 6(i-iv).

The galvanized steel specimens were degraded in the

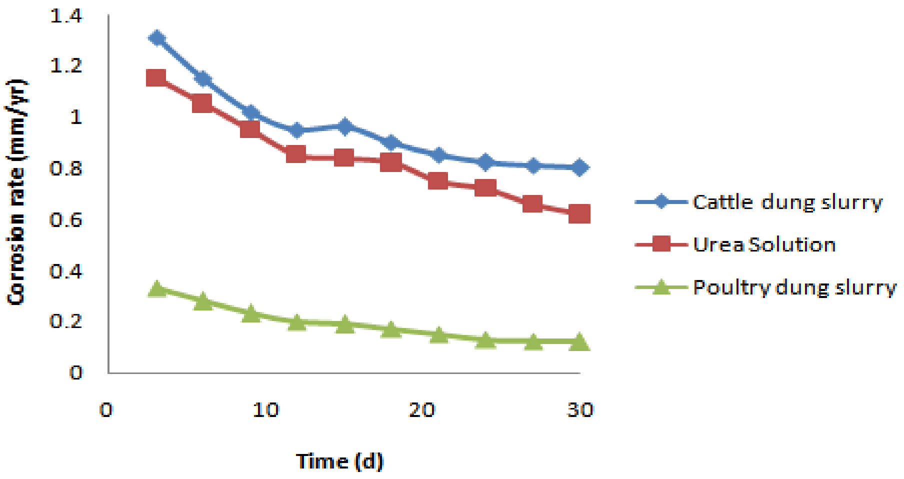


Figure 4. Variation of corrosion rate with time for the mild steel test specimens immersed in cattle and poultry dung/urine slurries and in urea.

Table 1. Corrosion of galvanised and mild steels in cattle dung/urine slurry.

Exposure time (Days)	Weight-loss (mg)		Corrosion rate (mm/yr)	
	Galvanised steel	Mild steel	Galvanised steel	Mild steel
3	5.8	35.8	0.0784	1.344
12	6.1	70.1	0.0246	0.657
27	7.2	238.7	0.0129	0.994

three different test media. In the cattle dung/urine slurry, Figure 5 (ii), the degradation was uniform in appearance thus indication a general corrosion phenomenon. It also presented the same corrosion form in the poultry dung/urine slurry, Figure 5 (iii). A clearer feature could not be obtained for the micrographs due to the very low power of the microscope that gave a maximum of x140 magnification in urea solution, a form of general corrosive surface degradation was also obtained for the test specimen (Figure 5(iv)).

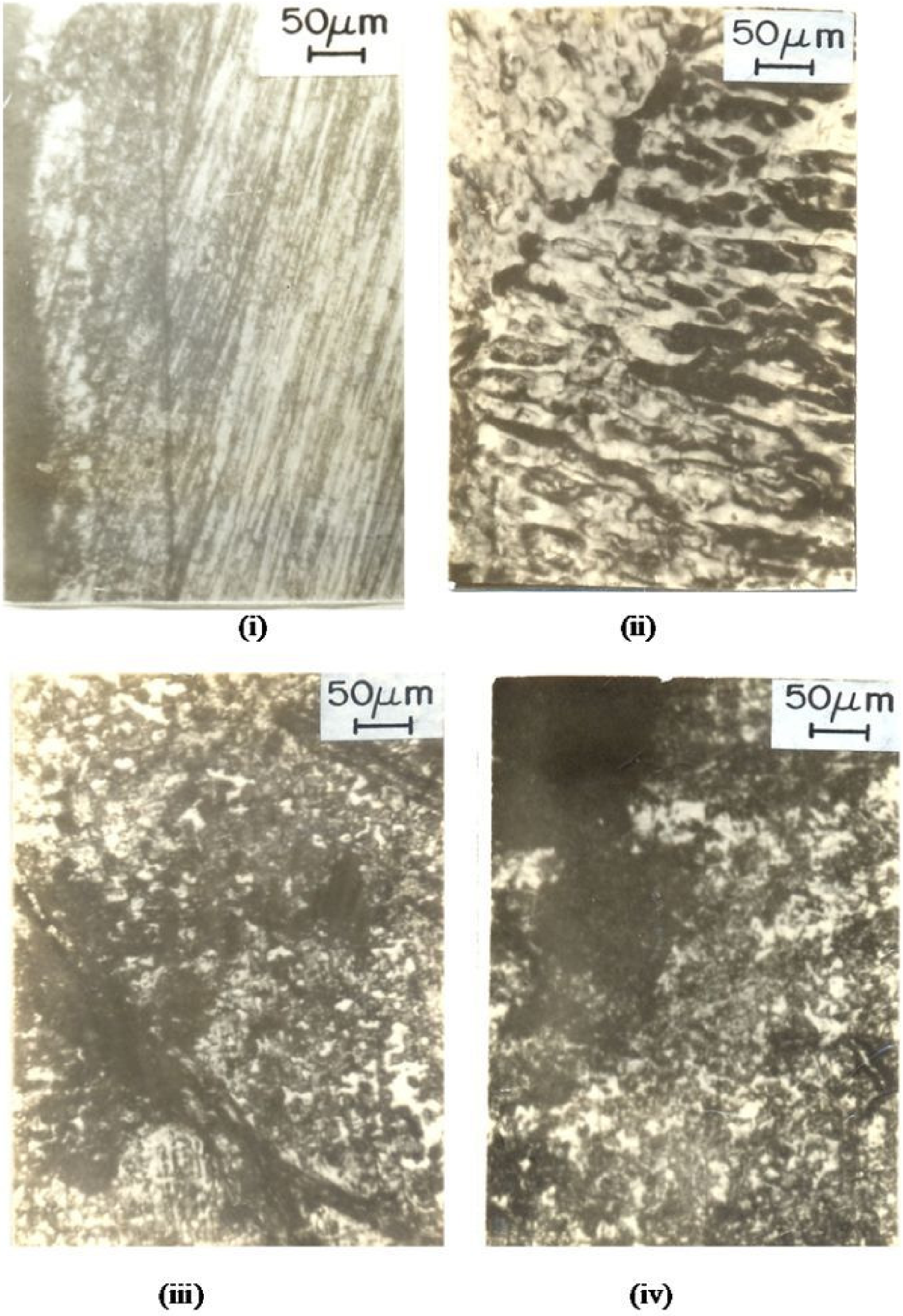
In Figure 6 (i-iv), the photomicrographs made of the surface of the mild steel test specimens before and after immersion in the different test media, are presented. In the cattle dung / urine slurry, Figure 6(ii), the mild steel specimen corroded uniformly. The poultry dung/urine slurry was also corrosive, Figure 6 (iii). The photo micrograph for the test specimen in urea solution is presented in Figure 6 (iv). It showed general corrosion with some scattered pits.

DISCUSSION

As previously mentioned in this work, the slurry used was a mixture of dung and urine in distilled water. The mixture is known to ferment to release moisture, ammonia and carbon dioxide. The reacting constituents in the slurries have been determined (Department of Industry) to be urea, uric acid, ammonia and ammonium salts, and naturally excreted chloride (common salt). In addition, the corrosive action of micro-organisms – bacteria in slurries such as above, could be significant.

The highest amount of weight loss and corrosion rate of both the galvanised and the mild steels in cattle dung/urine slurry recorded, Figures 1 to 4, indicated that the slurry contained more concentration of the corrosive constituents than the poultry dung/ urine slurry and apparently more than the urea solution. However, its urea content (undetermined) was assumed to be less than the amount of urea solution (0.5 M) that was separately used in the experiments. In addition, part of the released carbon dioxide (CO_2) during fermentation would have dissolved in the slurry to cause CO_2 corrosion in form of weak carbonic acid. The slurry constituents include the organic and inorganic sulphates. The presence of bacteria, which was also shown by the fouled medium and particularly, the sulphur oxidizing bacteria in the slurry could lead to the production of sulphuric acid. Desulphuvibrio, the most abundant anaerobic bacteria, are known to reduce sulphate to sulphide; for example:

$$S0_4^{2-}(aq) + 10H^+ + 8e\ (\text{bacterium}) \rightarrow H_2S\ (g) + 4H_2O_{(l)} \quad (1)$$



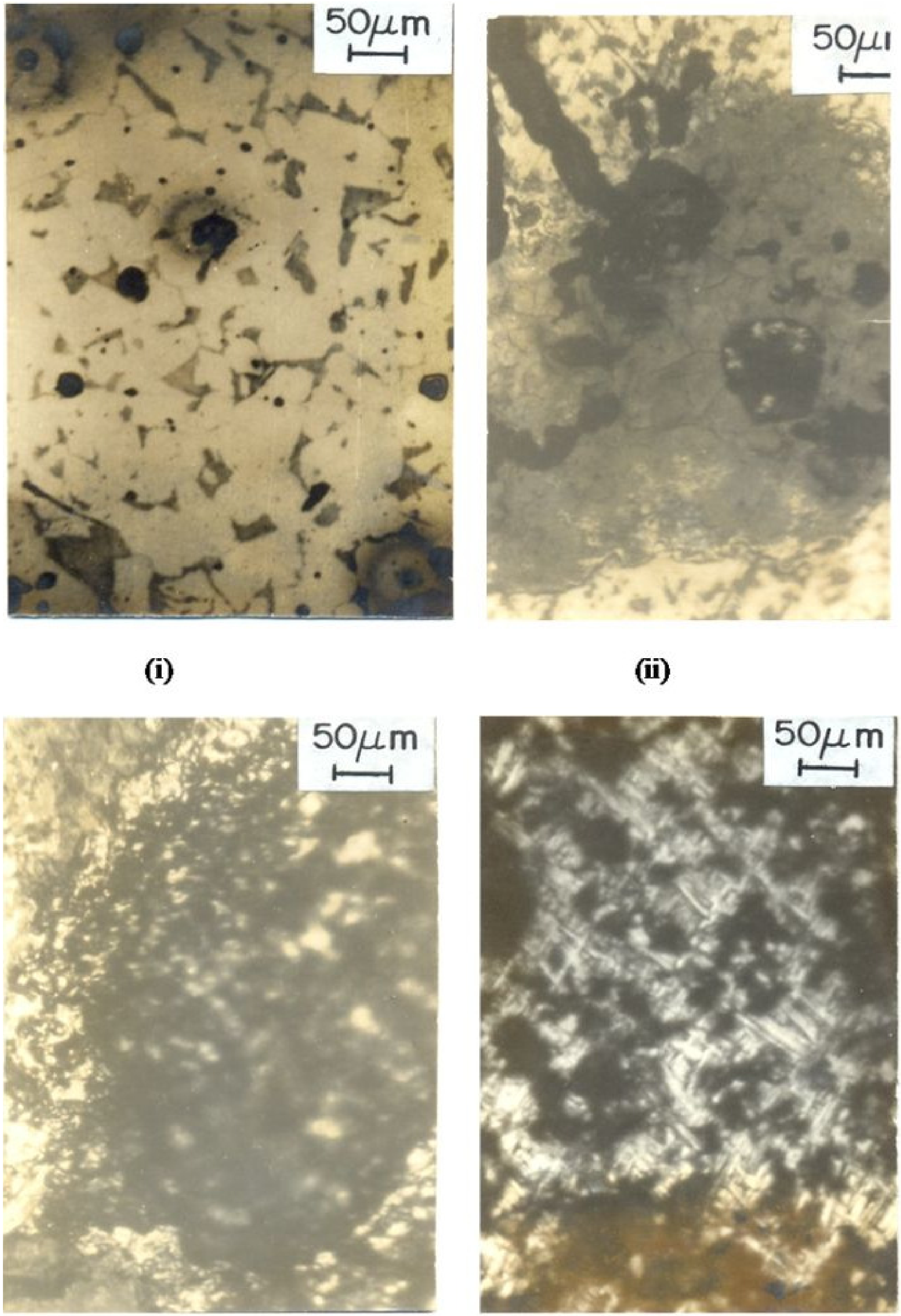
(i) (ii) (iii) (iv)

Figure 5. Photomicrographs of the galvanised steel test specimens before and after immersion in cattle and poultry dung/urine slurries and 0.5M urea solution. (x 140). (i) Before immersion (x 140); (ii) After immersion in cattle dung/urine slurry (x140); (iii) After immersion in poultry dung/urine slurry; (iv) After immersion in urea solution (x 140).

Another group of bacteria, use externally supplied oxygen to oxidise sulphur or sulphide to sulphuric acid, e.g.

$$S_{(s)} + 3/2O_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\ (aq)} \ldots\ldots\ldots\ldots \quad (2)$$

Sulphuric acid being corrosive would contribute to the higher corrosion of the test specimens in the cattle dung/urine slurry. The galvanised steel test specimen, however, has far better resistance to corrosion than the



(i) (ii)

(iii) (iv)

Figure 6. Photomicrographs of the mild steel test specimens before and after immersion in cattle and poultry dung/urine slurries and in 0.5M urea solution (x 140). (i) Before immersion (x 140); (ii) After immersion in cattle dung/urine slurry (x 140); (iii) After immersion in poultry dung/urine slurry; (iv) After immersion in urea solution (x 140).

mild steel in this test medium (Table 1).

This better resistance is due to the surface protection provided by the zinc coating. However, gradual dissolution of the zinc coating made the steel to be eventually slightly susceptible to corrosion. In fact, the weight loss recorded, emanated more from the loss of zinc coating on the steel substrate in the test medium rather than the anodic dissolution of the steel substrate itself. The mild steel corroded more than the galvanised steel. This was not unexpected since it (the mild steel) was not protected. It is believed that the corrosion resulted from the anodic dissolution of the steel specimen surface due to the interfacial chemical reactions occurring between the steel specimen and the test medium.

The urea (0.5 M) solution was less corrosive than the cattle dung/urine slurry (Figures 1 and 3). This corrosive behaviour is due to the test medium which contained only one type of reacting species urea, apart from water. The cattle dung/urine slurry contained several chemical constituents in comparison.

The galvanised steel specimen was more corrosion resistant in the urea than the mild steel. Again, the better corrosion resistance of the former than the latter is due to the protective coating of zinc on the steal substrate. This is a classic example of cathodic protection of steel. The zinc corrodes preferentially and protects the steel. The mild steel, on the other hand, could not form any other stable protective film to cover its surface and making it corrosion resistant.

Weight loss and corrosion rate of both the galvanized and the mild steels in the poultry dung/urine slurry was the lowest amount obtained in the test media. The reason for the least aggressive nature of this medium is difficult to explain. However, it might be that the corrosive constituents, earlier mentioned above, were present, in comparatively, very low concentration in the poultry - than in the cattle dung/urine slurries. The main constituent of the poultry dung/urine is uric acid. The concentration of this in the prepared slurry was probably insufficient to cause much corrosion attack of galvanised and mild steels. The variety and quantity of food and water intake of cattle, coupled with their more complex body nature could be associated with the more complex chemical constituents of cattle dung/urine than the poultry's.

Photomicrographs (Figures 5 and 6) made after the immersion of the test specimens in the different test media confirmed the surface corrosion degradation of the specimens.

Conclusion

The three test media used, that is, the cattle and the poultry dung/urine slurries and the urea solution are all corrosive to the galvanized and mild steels at the various degrees. The cattle dung /urine slurry was the most corrosive, closely followed by the urea solution. The poultry dung/ urine slurry was the least corrosive medium. The galvanised steel was more corrosion resistant in all the three test media than the mild steel test specimen.

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