

INHIBITION OF NST-44 MILD STEEL CORROSION BY SOME INORGANIC SUBSTANCES IN 0.1M AMMONIUM NITRATE SOLUTIONS

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Abstract. *This study presents the report of an investigation on the effect of sodium nitrite (NaNO_2), sodium biphosphate (Na_2HPO_4), potassium chromate (K_2CrO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) inhibitors on the corrosion characteristics of NST-44 mild steel in 0.1M ammonium nitrate solutions. The corrosion rates of the exposed mild steel were obtained using the weight loss immersion method. It was observed that oxidizing inhibitors like sodium nitrite, potassium chromate and potassium dichromate were more efficient than non-oxidizing inhibitors like sodium biphosphate and sodium benzoate by providing inhibition at molar concentrations of $5 \times 10^{-3}\text{M}$ and $5 \times 10^{-2}\text{M}$ respectively in 0.1M ammonium nitrate solutions. The results obtained on cold-work and various inhibitors indicate that cold working increased adsorption of inhibitors. Smaller quantities of inhibitors were therefore needed to inhibit corrosion of cold-worked mild steel than in un-worked sample. The results of this research are expected to improve the corrosion resistance of this steel as a constructional material for fertilizers, dyes and explosives processing industries in Nigeria.*

Keywords: Corrosion, Inhibitors, Mild Steel, Nitrate Solutions.

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INTRODUCTION

The manufacture of nitrogenous fertilizers, dyes and explosives are processes in which machineries or equipments are subjected to aggressive media (nitrate, sulphate). In such cases, conditions must be created so as to minimize the dissolution of the base metal after product removal. This can be achieved solely with the use of acid-corrosion inhibitors, which are mostly

inorganic compounds (Graham and John, 1984, Tuan and Xianming, 2009, Alagbe, 1997). Inhibition efficiencies of inorganic substances are shown to be related to inhibitor concentration, structure, molecular volume, degree of adsorption on the metal surface, pH, temperature and degree of deformation. Inhibitors have been grouped (Loto and Mohammed, 2000, Alagbe et al 2006, Fontana and

Greene, 1978, Evans 1961) into two main types namely:

- * Anodic inhibitors, which modify the anodic reactions and
- * Cathodic inhibitors which affect the cathodic reactions.

Another group of inhibitors may form an assorted screen over corrosion sites and may therefore be classified as adsorption inhibitors. These inhibitors can act either on the anodic or cathodic sites. Anodic inhibitors restrain the reaction at the anode by forming insoluble substance at the anodic sites. Chromate, nitrites and sodium benzoate have been shown to behave in this way (Pryor and Cohen, 1952). If present in sufficient amount such inhibitors are known to suppress corrosion. They are liable to cause localized attack and increase corrosion rate if an insufficient quantity is used. For this class of inhibitors the adsorption and subsequent growth of the insoluble products will be important parameters to be considered. This paper presents results on the effect of some inhibitors on mild steel.

Finally an attempt has been made to study the effect of cold-work and various inhibitors on the corrosion behaviour of this mild steel in nitrate solutions.

MATERIALS AND METHOD

The NST – 44 mild steel test specimen used had a percent nominal composition of 0.15C, 0.22 Si, 0.04S, 0.50Mn, 0.04P, 0.10Cr, 0.10Ni, 0.04Sn, 0.25Cu and 0.11N, the rest being Fe. A cylindrical steel rod was cut into short pieces having a cross section of 5mm and a gauge length of 40mm and their surfaces were given similar finish in order to descale them. They were then ground with 240, 320, 400 and 500 grits silicon carbide abrasive paper, cleaned thoroughly, rinsed in ultrasonic cleaner, dried. Before weighing, the specimens were left in the desiccators for 2 days to allow the oxide film on the surface reach steady state. Different concentrations (0.00005M, 0.0005M, 0.005M, 0.05M and 0.5M) of different inhibitors were prepared and added to 200ml of 10^{-1} M/ NH_4NO_3 (Ammonium nitrate). Another preparation of the 200ml of 10^{-1} M/ NH_4NO_3 (Ammonium nitrate) was made separately without the addition of any of the inhibitors. This serves as a control media. Specimens were washed in distil water, degreased in benzene, dried and weighed prior to taking the initial weights, thereafter they were immersed totally in 200ml of stagnant solutions containing mixtures of different concentrations of inhibitors in 10^{-1} M/ NH_4NO_3 (Ammonium nitrate).

Inhibition of Nst-44 Mild Steel Corrosion by some Inorganic Substances in 0.1M Ammonium Nitrate Solutions

The procedure was repeated for the environments without inhibitor. The duration of the test was 10 days. Each test was done in triplicate to set a result representative of the entire material. At the end of the test period (10days) the corrosion product formed on the surface of the specimen was removed by scrubbing under running water using fine rubber bung. After rinsing with methanol, the specimens were dried and then re-weighed. Curves of corrosion rates in Mils per Year (MPY) versus the concentration of the inhibitions (M) were plotted for the medium after 10 days of exposure. To investigate the effect of cold-work on the inhibitive properties of the various inhibitors, the torsion test pieces were machined on the lathe machine. Each has a gauge length of 90mm and a cross section of 5mm. The specimens were then cold worked by using torsion testing machine to 0%, 30% and 70% deformations. The torsion test pieces were then cut into short pieces having a cross section of 5mm and a gauge length of 40mm. They were washed with distil water, degreased in benzene and dried. Before weighing, the specimens were left in the desiccators for 2 days to allow the oxide films on the surface reach steady state. Specimens were weighed in turn and their original weights recorded. They were then totally immersed in 200ml of stagnant solutions containing mixture of different concentrations of inhibitors in

$10^{-1}\text{M}/\text{NH}_2\text{NO}_3$ (Ammonium nitrate). After 5 days immersion, the specimens were removed, scrubbed under running water with fine rubber bung to remove the corrosion products dried properly and re-weighed. The solution was kept at room temperature throughout the duration of the experiments. Curves of corrosion rates in Mils per Year (MPY) versus concentrations of inhibitor (M) after 5 days of exposure were plotted for each inhibitor with various percent deformations in the media.

RESULTS AND DISCUSSION

Effect of Inhibitor Concentration

The relationships between corrosion rate in Mils per Year (MPY) and the molar concentrations of inhibitors of NST-44 mild steel in $10^{-1}\text{M}/\text{NH}_4\text{NO}_3$ (Ammonium nitrate) are shown in fig. 1. The curves of the figure show that in nitrate solution, a very slight increase in corrosion rate occurs at low concentration of NaNO_2 (Sodium nitrite). While $\text{k}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate), k_2CrO_4 (Potassium chromate) and Na_2HPO_4 (Sodium biphosphate) all show greater increase in corrosion rate at low inhibition concentrations. $\text{C}_6\text{H}_5\text{COONa}$ (Sodium benzoate), shows a continuous fall in corrosion rate even at low concentrations. Nitrites are more inhibitive than chromates because they yield ammonia as a cathodic reduction product, a soluble substance which itself

may exert inhibitive properties in stagnant solution. The oxidizing inhibitors, NaNO_2 (Sodium nitrite), $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate) and K_2CrO_4 (Potassium chromate) are more efficient than the non-oxidizing $\text{C}_6\text{H}_5\text{COONa}$ (Sodium benzoate) and Na_2HPO_4 (Sodium biphosphate) by providing inhibition at molar concentrations of $5 \times 10^{-3}\text{M}$ and $5 \times 10^{-2}\text{M}$ respectively. This is because oxygen itself can exert inhibitive power by aiding repassivation, and thus lower concentrations of oxidizing inhibitors, which can supply their own oxygen, are needed than the non-oxidizing inhibitors which cannot. Alternatively, it may be that these oxidizing inhibitors are more easily adsorbed than the non-oxidizing ones. The increase in corrosion rates for NaNO_2 (Sodium nitrite), $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate) and Na_2HPO_4 (Sodium biphosphate) at low concentration may be due to their inability to plug all corrosion sites effectively. This ineffective coverage might have resulted in large cathodic sites compared with small areas of anodic sites. Sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) does not cause an increase in corrosion rates at low inhibitor concentrations, but a steady drop in corrosion with increase in molar concentration of inhibitor. The reason is that attack in the presence of small quantity of inhibitor is still widespread

and uniform instead of being localized as in the case of other inhibitors.

Effect of Cold-Work

The effects of cold-work on the inhibitive properties of NaNO_2 (Sodium nitrite), Na_2HPO_4 (Sodium biphosphate) and $\text{C}_6\text{H}_5\text{COONa}$ (Sodium benzoate) in $10^{-1}\text{M}/\text{NH}_4\text{NO}_3$ (Ammonium nitrate) on mild steel are shown in figs. 2-4. Fig. 2 shows that there is a decrease in corrosion rate as inhibitor concentrations increase for specimens given 0%, 30% and 70% deformations. However, at inhibitor concentration of $5 \times 10^{-4}\text{M}$ of NaNO_2 (Sodium nitrite), the corrosion rate increased with little degree of cold deformation (30%). Beyond some critical inhibitor concentration, corrosion rate decreased for both deformed and undeformed specimens. The amount of inhibitor required for complete or almost suppression of corrosion was least for 30% deformation, followed by 0% deformation and finally for 70% deformation. For example, at $5 \times 10^{-3}\text{M}$ of NaNO_2 (Sodium nitrite) nearly complete inhibition was observed in specimen given 30% deformation where as nearly complete inhibition was only observed at $5 \times 10^{-2}\text{M}$ of NaNO_2 (Sodium nitrite) for specimens given 0% and 70% deformations. At low inhibitor concentration, a certain degree of cold-

Inhibition of Nst-44 Mild Steel Corrosion by some Inorganic Substances in 0.1M Ammonium Nitrate Solutions

work is beneficial because adsorption occurs readily on the slip steps created.

As the amount of inhibitor increases however, film growth and repassivation of film become the dominant factor. At higher inhibitor concentration (above $5 \times 10^{-3} \text{M}$ of NaNO_2) every specimen becomes more resistant to corrosion despite the increase in anodic sites created on the deformed material. This may be due to better adhesion on the oxide film on the newly created slip steps as compared to adhesion of existing film on the undeformed materials. Figs 3 and 4 show the results of Na_2HPO_4 (Sodium biphosphate) and $\text{C}_6\text{H}_5\text{COONa}$ (Sodium benzoate) inhibitors respectively. At low concentration, cold-work encouraged inhibition. This can be explained again in terms of better adsorption of inhibitors on the slip steps created by cold-work. Beyond $5 \times 10^{-5} \text{M}$, however, the corrosion rate increased with deformation up to $5 \times 10^{-4} \text{M}$ of Na_2HPO_4 (Sodium biphosphate) after which a drop was observed. Fig.3 shows the same pattern as fig.4. The rise in corrosion rate with increase in cold-work and inhibitor concentration may be due to the surface of the material. Since adsorption occurs readily on the cold-worked material, the film may grow rapidly and break after a limited thickness is active due to non-plasticity of the oxide. Soluble complexes may also be formed at the pores of the

film which render film unprotective. The high-energy zones in the deformed material may render film unprotective. The breakdown of the protective film at high inhibitor concentration may be viewed as follows. Ferrous ions are first oxidized to ferric hydroxide or oxide by the inhibitor. The effectiveness of the inhibitors within the pores is reduced leading to a reduction in pH. The acidity within the pores may become sufficiently high as to allow the corroding metal at the pore base to appear as soluble product. The breakdown of the film is assumed to occur only after a certain thickness might have been exceeded. As inhibitor concentration is increased further, however, the nitrate ion-inhibitor ratio decreases within the pores and breakdown process is again suspended and a reduction in corrosion rate is observed as in figs. 3 and 4. Thus in figs. 3 and 4 the initial drop in corrosion rate at low inhibitors concentration and cold-work is controlled by the properties of the surface film, while the final drop is controlled by the nitrate-ion inhibitor ratio.

CONCLUSIONS

- The main conclusions drawn from this investigation were:

The corrosion of mild steel in 0.1M ammonium nitrate solutions can be inhibited by sodium nitrite (NaNO_2), sodium biphosphate (Na_2HPO_4),

potassium chromate (K_2CrO_4), potassium dichromate ($K_2Cr_2O_7$) and sodium benzoate (C_6H_5COONa), to varying degrees.

- The inhibitive power in 0.1M ammonium nitrate solutions decreased in the following ranking order. $NaNO_2$, $K_2Cr_2O_7$, K_2CrO_4 , C_6H_5COONa and Na_2HPO_4 .
- The oxidizing inhibitors like sodium nitrite, potassium dichromate and potassium chromate were more efficient than non-oxidizing inhibitors like sodium biphosphate and sodium benzoate by providing inhibition at molar concentrations of $5 \times 10^{-3}M$ and $5 \times 10^{-2}M$ respectively in 0.1M ammonium nitrate solutions.
- A little cold-work improved the inhibitive powers of sodium nitrite, sodium biphosphate and sodium benzoate especially at low concentrations. This was attributed to an increase in adsorption of inhibitive ions on the created slip steps. Excessive amount of cold-work was found to have a detrimental effect especially at high concentrations of sodium biphosphate.

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Inhibition of Nst-44 Mild Steel Corrosion by some Inorganic Substances in 0.1m Ammonium Nitrate Solutions

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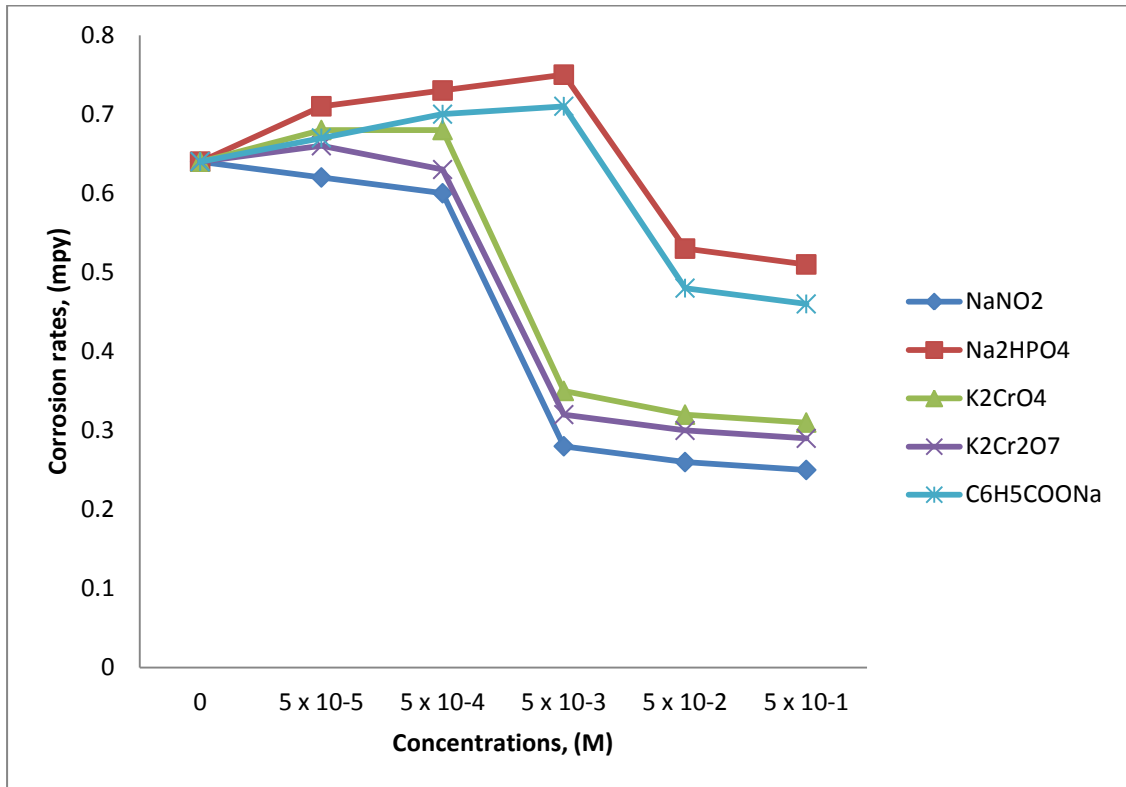


Figure 1 Relationship between corrosion rates and concentration of inhibitors after 10 days of exposure in $10^{-1}M/NH_4NO_3$

Inhibition of Nst-44 Mild Steel Corrosion by some Inorganic Substances in 0.1m Ammonium Nitrate Solutions

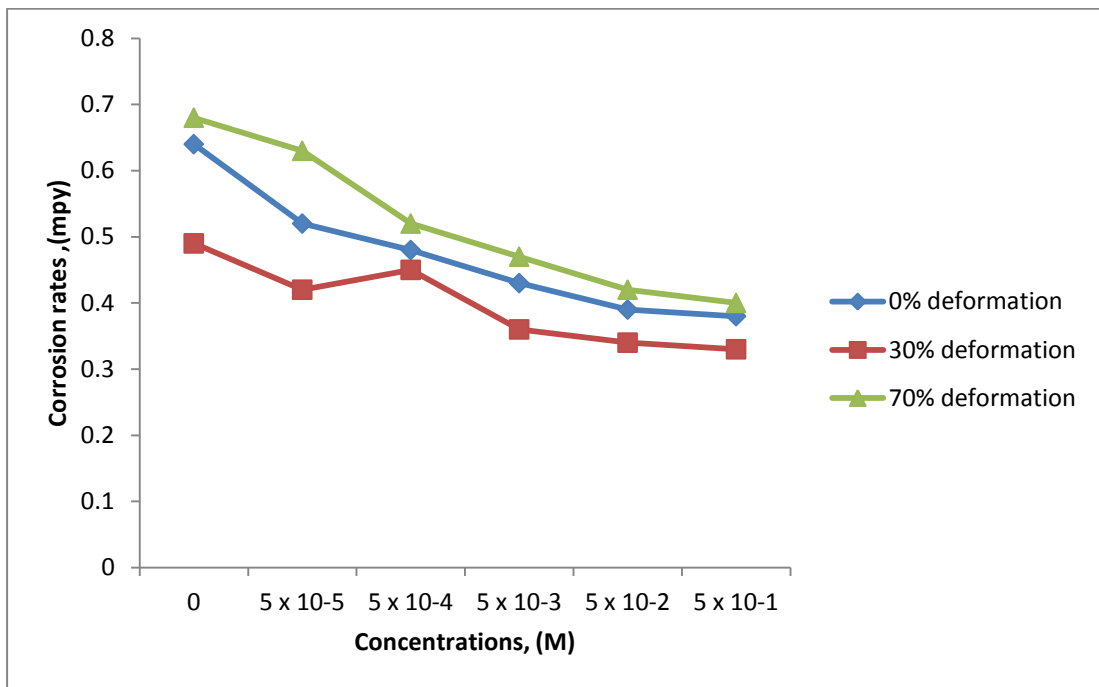


Figure 2 Relationship between corrosion rates and concentrations of NaNO₂ in 10⁻¹M/NH₄NO₃ for material given different percent deformations after 5 days of exposure.

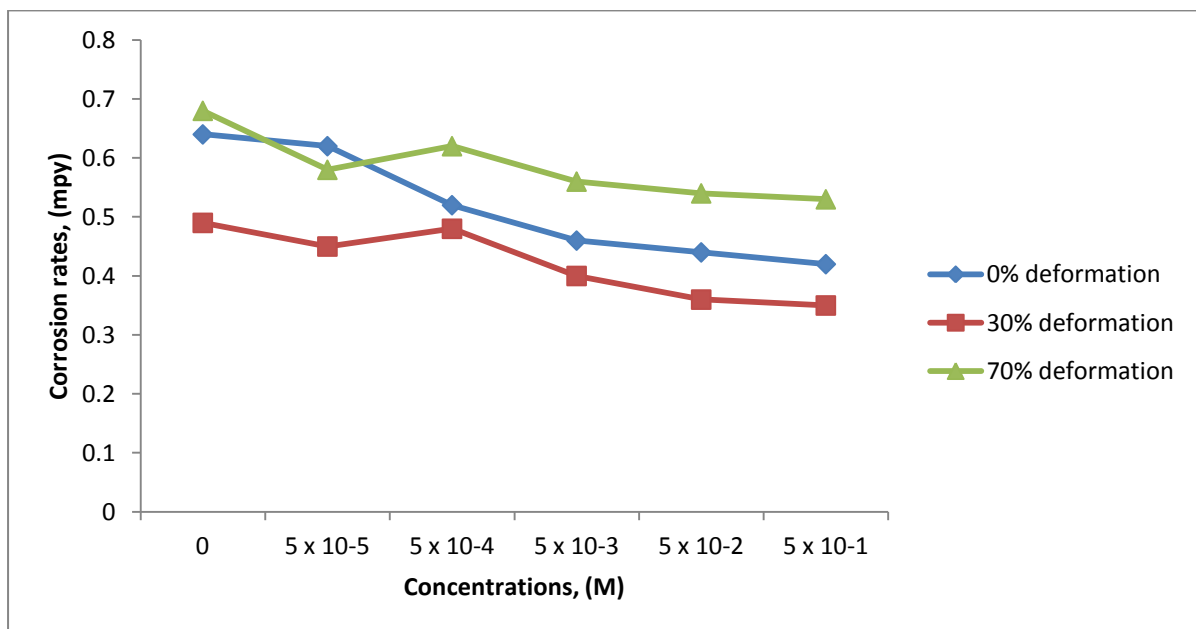


Figure 3 Relationship between corrosion rates and concentrations of Na₂HPO₄ in 10⁻¹M/NH₄NO₃ for material given different percent deformations after 5 days of exposure

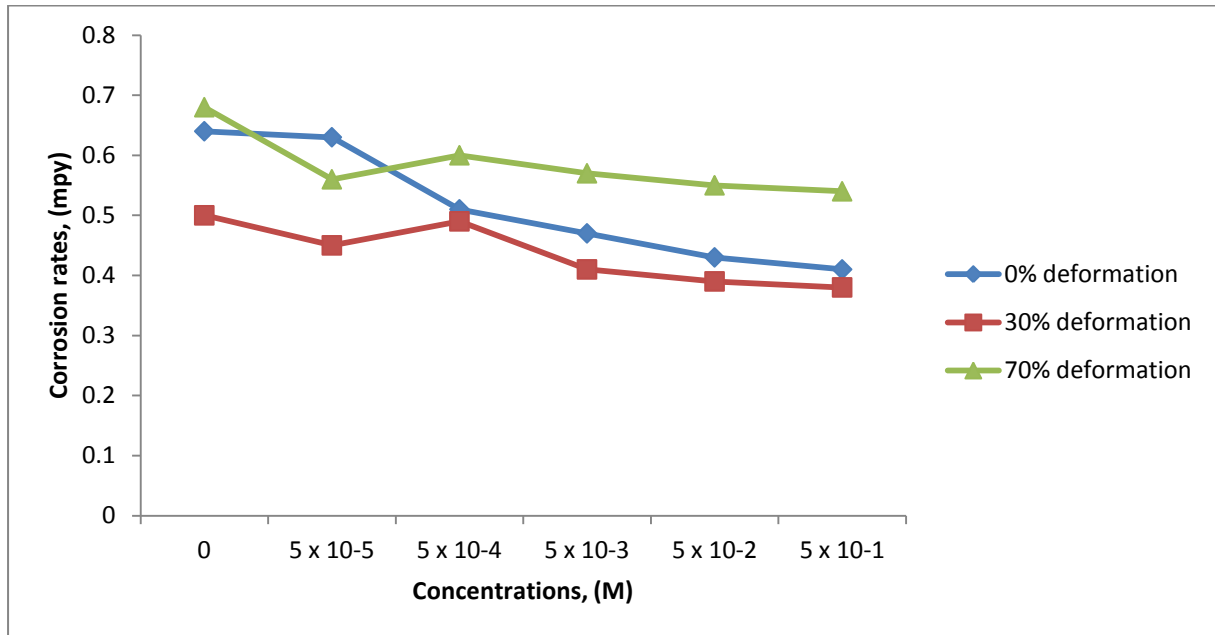


Figure 4 Relationship between corrosion rates and concentrations of C_6H_5COONa in $10^{-1}M/NH_4NO_3$ for material given different percent deformations after 5 days of exposure