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NASA Technical Memorandum 82935

(NASA-TM-82935) FRICTION AND WEAR OF IRON
AND NICKEL IN SODIUM HYDROXIDE SOLUTIONS
(NASA) 23 p HC A02/MF A01 CSCL 11F

N83-10171

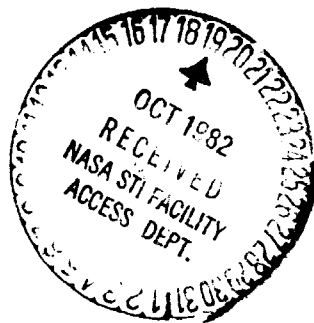
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Friction and Wear of Iron and Nickel in Sodium Hydroxide Solutions

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Prepared for the
Joint Lubrication Conference
cosponsored by the American Society of Mechanical Engineers
and the American Society of Lubrication Engineers
Washington, D.C., October 5-7, 1982

NASA

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Summary

A loaded spherical aluminum oxide rider was made to slide, while in various solutions, on a flat iron or nickel surface reciprocating a distance of 1 cm. Time of experiments was 1 hr during which the rider passed over the center section of the track 541 times. Coefficients of friction were measured throughout the experiments. Wear was measured by scanning the track with a profilometer. Analysis of some of the wear tracks included use of the SEM (scanning electron microscope) and XPS (X-ray photoelectron spectroscopy). Investigated were the effect of various concentrations of NaOH and of water.

On iron, increasing NaOH concentration above 1.11 N caused the friction and wear to decrease. This decrease is accompanied by a decrease in surface concentration of ferric oxide (Fe_2O_3) while more complex iron-oxygen compounds, not clearly identified, also form. At low concentrations of NaOH, such as 1.11 N, where the friction is high, the wear track is badly torn up and the surface is broken. At high concentration, such as 11 N, where the friction is low, the wear track is smooth. The general conclusion is that NaOH forms a protective, low friction film on iron which is destroyed by wear at low concentrations but remains intact at high concentrations of NaOH.

Nickel behaves differently than iron in that only a little NaOH gives a low coefficient of friction and a surface which, although roughened in the wear track, remains intact. With water alone, the track is torn up and broken although the friction is very little higher than in the NaOH solutions. It may be that it takes less NaOH to form a protective film on nickel than iron.

*This paper is an extension of the work reported in NASA Technical Paper 1985, "Friction and Wear of Iron in Corrosive Media".

Introduction

Corrosion is recognized as an important variable in the friction and wear of metals (ref. 1). Still the role of corrosion is not well understood. Most studies have been concerned with specific practical problems, such as the use of anti-corrosion material in lubricants (ref. 2) or moving parts in body implants (ref. 3). However, general basic knowledge is missing.

The effects of corrosion are complex. There is the possibility of general attack with no particular effect in the wear contact region. However, the wearing region is different, electrochemically, than the surroundings. It contains metal which is cold worked, metal which is being highly stressed elastically as well as plastically, and metal which is at locally high temperatures at shearing points (refs. 4 and 5). Electrochemical potentials might be established locally to either impede or enhance corrosion. Furthermore, high cyclic stresses may promote stress corrosion and corrosion fatigue (ref. 6).

Resistance to corrosion is often the result of formation of some type of film on the metal. Wear can destroy such films. Alternatively, wear could develop better corrosion resistant films by producing new surfaces. Furthermore, the coefficient of friction is, like corrosion resistance, highly sensitive to surface films.

The objective of this study was to start a systematic investigation of the role of corrosion in the friction and wear of metals.

In the studies reported here, the "corrosive" solutions were various concentrations of NaOH. Although neither iron nor nickel are strongly corroded by NaOH at room temperature, plain carbon steels are susceptible to "caustic embrittlement." This embrittlement is now recognized to be a "stress

corrosion" process. Furthermore, stress corrosion appears to be associated with the breakdown of protective corrosion films. The reasonableness of including NaOH solutions as a corrosive environment was soon established by showing a strong sensitivity of friction effects on iron to concentration of the solutions. Nickel, another metal which strongly resists over-all attack by NaOH, was later added to the study.

Materials

The iron used in these studies was better than 99.99 percent pure and was fully annealed. Its hardness was 40 Rg. The nickel was electrolytic which had been annealed to a hardness of 30 Rg.

The water used in the experiments and used in making solutions was deionized and distilled. It was treated to control dissolved oxygen by one of three methods:

1. Vacuum degassing
2. Saturated by bubbling air through it at room temperature
3. Degassed by boiling while bubbling argon through the water

The results of these treatments are discussed. The NaOH used to make solutions was certified A.C.S. electrolytic pellets.

Apparatus

The apparatus used in this investigation is shown schematically in Figure 1. The rider was an aluminum oxide (sapphire) ball 6 millimeters in diameter, mounted in a holder.

Most of the specimens were irregularly shaped pieces of flat iron or nickel mounted with an epoxy cement onto a fiberglass-plastic holder. The holder was held by a vise in the jig which was moved reciprocally under the rider. The holder kept the solution spilled off the top of the specimen surface from flowing into the unit and with a shield prevented spattering of the solution during a run.

Since these specimens could not be used in high-vacuum systems, short stainless steel cylinders with a size (10 mm diameter) to fit into the holders for the SEM and XPS units, were attached to the bottom of flattened and annealed pieces of high purity iron or nickel with an epoxy developed for use in high vacuum. A wire was then spot welded to the side of the specimen and the cylinder to make electrical continuity.

As indicated in Figure 1, the mounted iron specimens held in the jig were moved back and forth under the loaded rider. The motion of the specimen was 10 millimeters in each direction, but the length of the track was shorter. The track length varied somewhat because of the friction at the end of each reversal. The rider usually carried a load of 250 grams; less for some experiments. The arm holding the rider was flexible so that the friction force (F) could be measured with the aid of calibrated strain gauges and continuously recorded.

There were nine reversals per minute (i.e., the flat specimen travelled at an average speed of 9 cm/min) and each experiment was carried out for 60 minutes. Thus, the rider passed over the center section of the track 540 times (270 times each way) during an experiment. The center section of the track was studied in this work.

The apparatus was housed in a closed plastic box in which a positive flow of argon gas was maintained during experiments with low-oxygen solutions. The cover was left open when the solutions were saturated with air.

Experimental Procedure

The iron or nickel flats were metallographically ground through 600-grit silicon carbide paper. They then were polished with diamond paste, first 6 micrometer paste (sometimes skipped) then 3 micrometer paste. Final polishing

was with 0.3 micrometer alpha alumina on a flooded flat polishing wheel. The polished specimen was cleaned with a strong flow of tap water, and dried with ethanol. The dried specimens were etched until the disturbed metal was removed and the grain structure was visible. For iron the etchant was 5 percent nital, and for nickel it was 1 part nitric acid to 1 part acetic acid (glacial). The specimen was then lightly polished with the 0.3 micrometer alumina, washed with a strong flow of tap water and dried with ethanol.

In the individual experiments, the mounted specimens were clamped into the jig in the box. The rider was lowered to about 4 millimeters above the surface of the iron or nickel. Several drops of the desired solution were squirted under the rider and on the surface near the rider to form one large drop covering most of the surface of the specimen. The rider was lowered through the drop until a strain gauge showed that it just touched the iron surface. When this was accomplished, the weight was loaded onto the rider and sliding initiated.

The drop of liquid immediately formed a meniscus between the holder of the rider and the iron or nickel surface and remained there during the course of each experiment. Thus, the rider and its point of contact with the specimen were always in the interior of a large liquid drop. Furthermore, the meniscus provided a continuous supply of solution to keep the rest of the iron wet in and near the wear track.

Friction force of the rider moving across the iron in the wear track, was recorded continuously from the output of strain gauges on the flexible arm that held the loaded rider. The coefficient of friction then, was the force divided by the load on the rider. The static coefficient μ_s was the maximum F in each direction of travel, or as used, half the maximum force in a complete reversal of travel. The kinetic coefficient was estimated in the usual manner

of using the force as the mean between the maximum force (stick) and the minimum force (slip) when stick-slip occurred (ref. 5).

All specimens except those prepared for SEM and XPS studies were scanned across the track by a surface profilometer to estimate wear characteristics.

XPS Procedure

Details of the X-ray photoelectron spectroscopy (XPS) were used to analyze wear surfaces generated during the friction and wear experiments and can be found in reference 7.

To obtain reproducible results, strict standardization of the order and time of recording was used. The instrument was regularly calibrated. The analyzer work function was determined by assuming the binding energy for the Au 4f 7/2 peak to be 83.8 electron volts. That is, the gold 4f 7/2 peak was used as the reference line. All survey spectra (scans of 1050 or 1100eV) were taken at a pass energy of 50 or 100 electron volts, and this provided the instrumentation resolution of 1 electron volt at room temperature. The magnesium K α X-ray was used with an X-ray source power of 400 watts (10 kV, 40 mA). The narrow scans of the carbon 1s, silicon 2p, and oxygen 1s peaks were just wide enough to encompass the peaks of interest and were obtained with a pass energy of 25 electron volts at room temperature.

To evaluate the charging effect and to determine accurately the energy and shape of peaks, spectra were recorded several times. Resolution of the spectral peak is 1.56 electron volts full width. The energy resolution is 2 percent of the pass energy, that is, 0.5 electron volt. The peak maximums can be located ± 0.1 electron volt. The reproducibility of peak height was good, and the probability of error in the peak heights ranged from ± 2 percent to ± 8 percent. Peak ratios were generally good to ± 10 percent or less.

RESULTS AND DISCUSSION

Iron in Water

Reference experiments were conducted initially with water as the corrosive medium. The μ_s was reproducible, with values of 0.26, 0.29, and 0.30 being obtained. The friction coefficients for water can be classified as "moderate." Many solutions gave lower values; a few gave higher values.

An SEM photograph of the wear in water is shown in Figure 2a. Wear tracks obtained in water were easily seen in the light microscope and difficult to observe with the SEM. The SEM shows the track to be smooth. The ease of observation with reflected light probably results from the formation of a thin, dark surface oxide that provides contrast. If this conclusion is correct, water can be considered as corrosive under these conditions. The formation of the film could come from oxygen in the water, even though it had been purified and degassed. On the other hand, direct oxidation by water (steam) could have taken place at the local hot spots where shear occurs during sliding wear.

The top curve in figure 3 shows the profile of the specimen wear track obtained in water. A considerable amount of metal has been displaced to form a sharp lip at the edges of the wear track.

Iron in Sodium Hydroxide

The variation of the static coefficient of friction μ_s with NaOH concentration is presented in figure 4, and a comparable variation in the kinetic coefficient of friction μ_k in figure 5. In this NaOH system there is a maximum in μ_s at 0.01 N. At concentrations of NaOH higher than 0.01 N, the μ_s continuously dropped to around 0.17 and below as NaOH increased to 10 N or above.

An often important variable in corrosion is the amount of oxygen dissolved in the solution. Most of the data in figures 4 and 5 were obtained

with deionized distilled water which had been vacuum-degassed. Because of the possibility that oxygen in the water was important, some duplicate experiments were made at controlled high and low oxygen levels.

The high oxygen levels were obtained by bubbling air through the deionized distilled water at room temperature for 24 hours or more. This caused the water to contain 9 ppm oxygen, almost exactly the saturation level of the partial pressure of oxygen in air at room temperature and kept at that level during the test by keeping the box open to the atmosphere.

At the other extreme, oxygen was removed by bubbling argon through the distilled water while it was being boiled. This produced water with the low value of <0.5 ppm oxygen. Experiments were made in the argon chamber with freshly deoxygenated water. These experiments were made with the test chamber closed, and thoroughly purged with a high flow of argon.

Figure 4 shows no detectable difference in μ_s from variations in oxygen concentrations either at high or low concentrations of sodium hydroxide on iron. This tolerance for oxygen was helpful. The oxygen content of the vacuum degassed water was not monitored and it appears to have been variable. A later analysis showed 6.5 ppm O_2 which is near saturation in air.

The curve for μ_k vs NaOH concentration (fig 5) is generally parallel to the curve for μ_s . However, at 0.01 N NaOH, where μ_s was highest, there was no stick-slip.

From the standpoint of corrosion alone, steel, and presumably iron, is not attacked overall by any concentration of NaOH at room temperature. Still, NaOH is known for causing "caustic embrittlement" of steel. This problem has been known for over 100 years as a major cause of explosions in railroad and stationary boilers (refs. 8 to 10).

It is now known that caustic embrittlement is a classic case of stress corrosion failure (ref. 9). Overall corrosive attack is low. However, in regions under elastic strain, pitting and grain boundary attack occur. These progress by some mechanism and with applied or residual stresses lead to brittle fracture in accordance with the principles of fracture mechanics.

The iron in the track is certainly under a high local elastic stress when the rider passes over. It retains high residual elastic stresses because of local plastic deformation. This might be an area where the pitting and grain boundary attack inherent in caustic embrittlement start. This was observed with 0.001 N NaOH.

A region of the track showing grain boundary attack was examined under the light microscope. The bottom profilometer trace in figure 3 shows a deep pit. This pit was seen also in the light microscope.

Figure 2b shows a SEM photograph of the wear track made in the 0.01 N NaOH solution, which gave the highest friction, ($\mu_s = 0.47$). The surface profile track of a duplicate specimen ($\mu_s = 0.52$) shown in figure 3 (second curve from bottom) reveals that the center of the track was rough. Still, there was no evidence of deep pits and/or deep grain boundary attack as with some of the specimens generated in 0.001 N NaOH, as discussed previously. On the other hand the SEM photograph in figure 2b shows a severely broken and distorted wear surface.

It is suggested that a low-friction film tends to form but is broken down under the conditions encountered in these experiments. This exposes high-friction material (iron) from below the film. Furthermore, it is suggested that this surface film breakdown is related to the elastic stress conditions that cause the pitting and grain boundary attack characteristic of NaOH stress corrosion of plain carbon steel.

The high-friction and wear tracks in dilute NaOH can be compared with low-friction and wear tracks obtained in concentrated NaOH solutions. A concentrated 20 N solution, gave a μ_s of 0.17. Figure 2c shows an SEM photograph of a specimen obtained in one of these experiments. Note how smooth the wear track appears in the photograph, even at high magnification. The small amount of metal disturbed at this low friction is shown in the second profile in figure 3. Surely, under these conditions, a tenacious film forms that does not break up, and this film acts as a lubricant. That the amount of metal disturbed in the wear track is directly proportional to the μ_s when operating in NaOH is shown in figure 6.

Following this approach led to the idea that the load on the rider should have an important effect on μ_s . The thought was that a lighter load than the 250 grams regularly used in this study should not penetrate the surface layer in the wear track, thus leading to a reduction in μ_s . Then the coefficient of friction would rise again with lower loads, as is usually observed in this type of study.

This idea was not substantiated as is shown in figure 7. For both the high-friction condition of 0.01 N NaOH and the low friction condition of 10 N NaOH, μ_s increased noticeably as the load was reduced to as low as 20 or 50 grams.

Surface profile scans did not reveal the trace at the lowest loads. However, in the light microscope irregular patches appeared, indicating a thin corrosion-product buildup in the 0.01 N NaOH. Thus, it still appears that the slider disturbs a surface film and allows reaction with the 0.01 N NaOH even when the general surface is protected from corrosion.

Nickel in Water and in Sodium Hydroxide

Figure 8 presents μ_s for nickel in water and in various concentrations of NaOH between 0.001 N and 20 N. The data indicates a low coefficient of

friction under all of these conditions, consistent with nickel being highly resistant to corrosion by both water and NaOH. Furthermore, unlike steel, nickel is not known to be susceptible to stress-corrosion cracking.

The specimen of Figure 9a tested under water shows a highly torn and distorted surface in the wear track. Corrosion principles suggest that a tenacious film protects nickel from corrosion by water, but that this might be disrupted in the wear track.

The wear track in Figure 9b of nickel tested under 0.1 N NaOH is roughened and irregular, but the surface is not broken.

When nickel was tested under HNO₃ solutions, (work still underway), even a trace of NaOH left in the apparatus sharply reduced μ_s . This is additional evidence that NaOH forms a tenacious film on nickel.

The track produced on nickel under NaOH was shallow and irregular as tested with the surface profilometer. The difference in corrosion conditions in the wear track certainly was important in the differences in wear between iron and nickel.

XPS Analysis of Iron in Water and Sodium Hydroxide

Figure 10 compares XPS spectra for wear surfaces of iron in H₂O and in 0.01 N NaOH. Oxygen bonded directly to iron (as in Fe₂O₃) has an oxygen 1s peak at 530 eV. Figure 10a shows this peak is dominant in H₂O. It also shows it to be weaker than a peak at 532 eV in the 0.01 N NaOH. The oxygen peak at 532 eV is generally attributed to a bond involving hydrogen as well as iron, i.e. Fe-O-H such as in FeOOH. Thus it appears that Fe₂O₃ is the primary oxidation product in water, but the surface is different in NaOH.

Figure 10b appears also to indicate Fe₂O₃ as the oxidation product in water. However, note that in Figure 11 which superimposes the Fe₂O₃ spectra (ref. 11) on the 0.01 N NaOH spectra, shows a skewing and broadening of the

Fe₂O₃ curve toward the lower energy side. This suggests that FeO or some complicated compound involving ferrous oxide is also present.

Figure 12 indicates that not only is there a difference in XP analysis in water and 0.01 N NaOH, but varying the NaOH concentration varies the spectra.

Sodium was not detected in any scans between 1068 and 1082 e V with NaOH concentrations even up to 20 N.

More work is needed to unequivocally identify the oxidation products by XPS.

CONCLUSIONS

Based on the experimental results obtained in this investigation with iron and nickel examined in water and in NaOH of various concentrations, the following conclusions were drawn:

1. With increasing concentrations of sodium hydroxide (NaOH) beyond 0.01 N, the friction and wear to the iron surface decrease. This decrease is accompanied by a decrease in the surface concentration of ferric oxide (Fe₂O₃).
2. In addition to Fe₂O₃, more complex iron-oxygen compounds form on iron under sodium hydroxide solutions. The corrosion-wear product is not yet clearly identified.
3. In low concentrations of NaOH, such as 0.01 N, where the friction is high, the wear track is badly torn up and the surface is broken. At high concentrations, such as 10 N, where the friction is low, the wear track is smooth.
4. The general conclusion is that NaOH forms a protective, low friction film on iron which is destroyed by wear at low concentrations but remains intact at high concentrations of NaOH.

5. Nickel behaves differently than iron in that only a little NaOH gives a low coefficient of friction and a surface which, although roughened in the wear track, remains intact. With water, in the absence of NaOH, the wear track is torn up and broken, although this gives only moderately more friction than the NaOH solutions. It may be that it takes much less NaOH to form a protective, low friction film on nickel than on iron.

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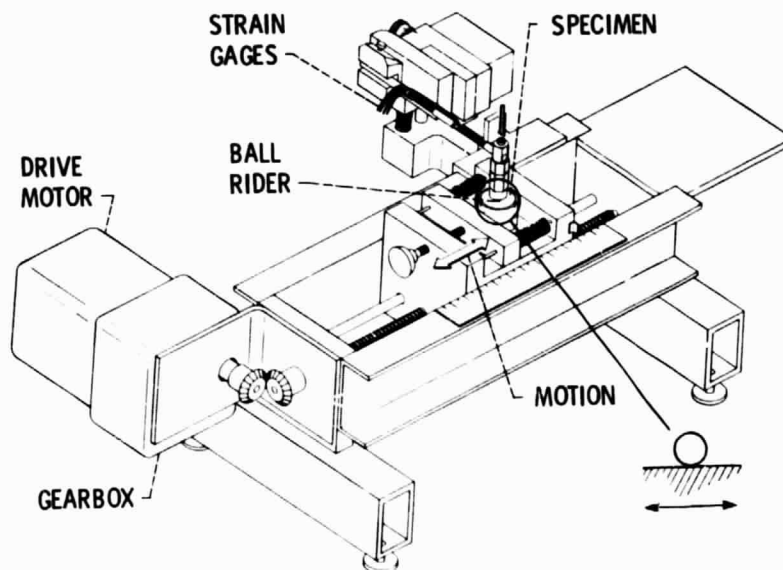
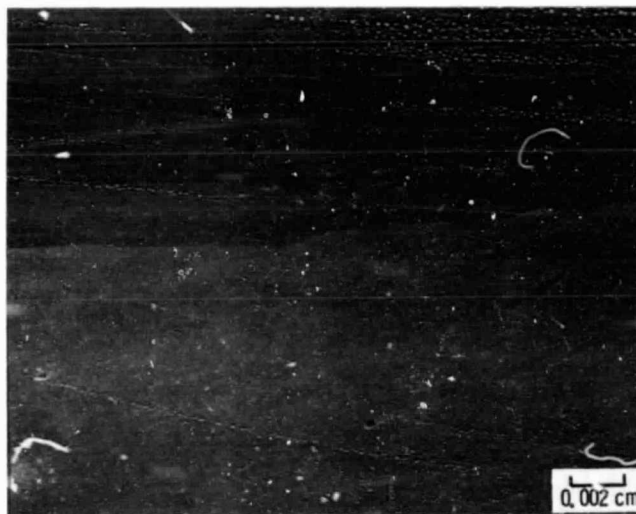
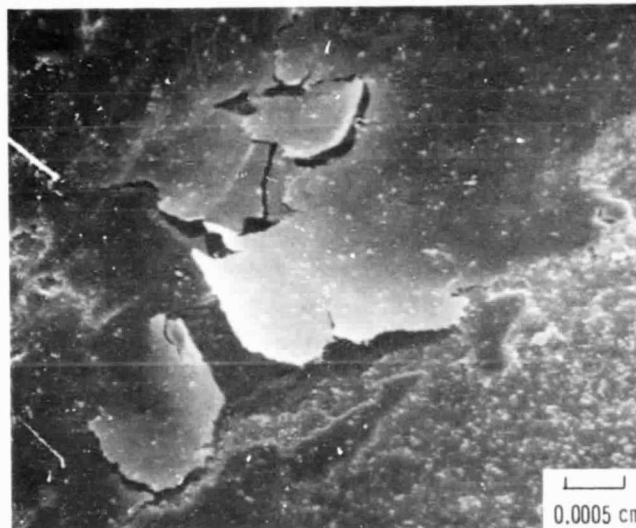


Figure 1. - Friction and wear apparatus.

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(a) Water
 $\mu_s = 0.30$
(Wear track
is at top of
photograph)



(b) 0.01 N NaOH
 $\mu_s = 0.47$



(c) 20 N NaOH
 $\mu_s = 0.17$

Figure 2. - SEM photographs of wear tracks made with NaOH and with water on iron.

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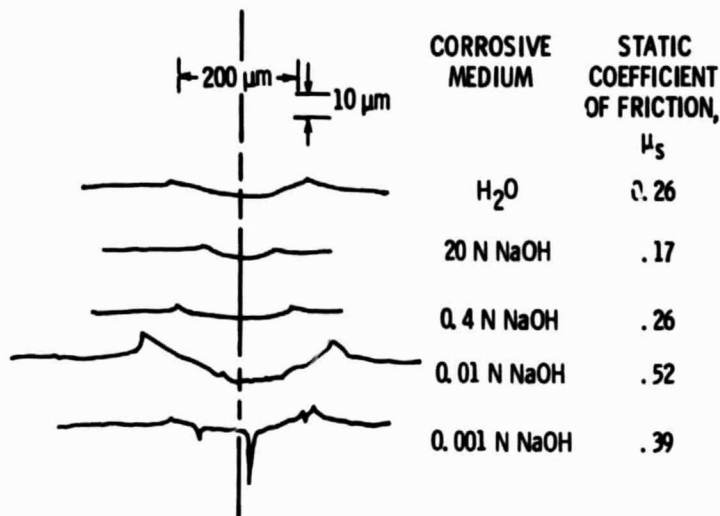


Figure 3. - Profilometer traverses across wear tracks generated by Al₂O₃ ball sliding on iron flat in various media. (Wear tracks were made on the iron flat.)

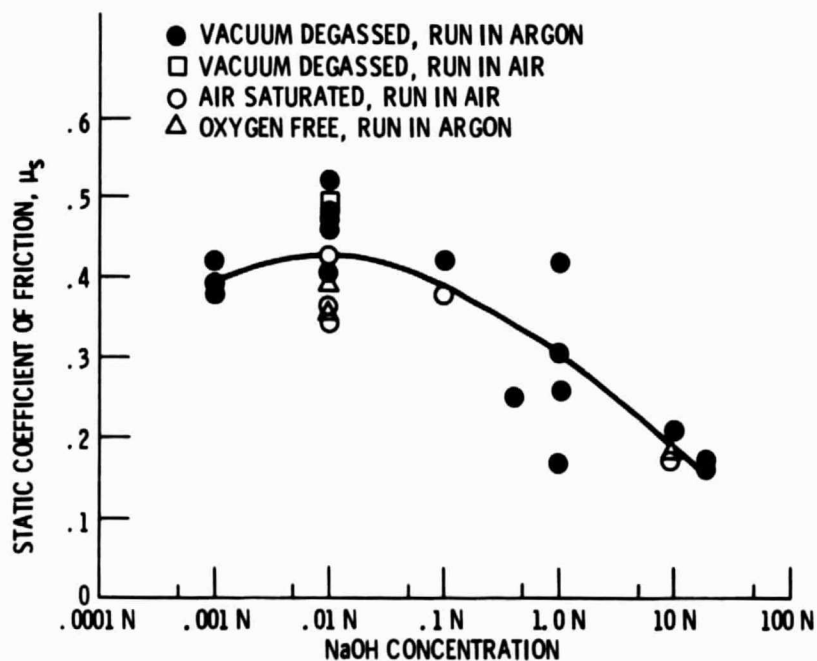


Figure 4. - Effect of NaOH concentration on the static coefficient of friction for Al₂O₃ ball sliding on iron in NaOH solutions.

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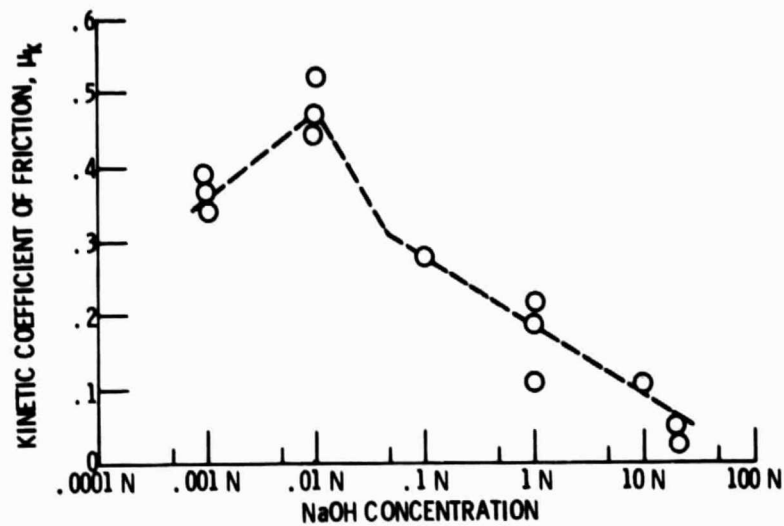


Figure 5. - Effect of NaOH concentration on kinetic coefficient of friction for Al_2O_3 sliding on iron flat in NaOH solutions.

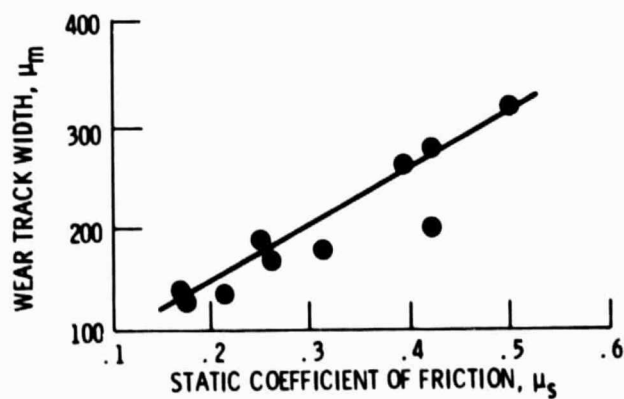


Figure 6. - Relation between wear track width and static coefficient of friction for Al_2O_3 ball sliding on iron flat in NaOH solutions.

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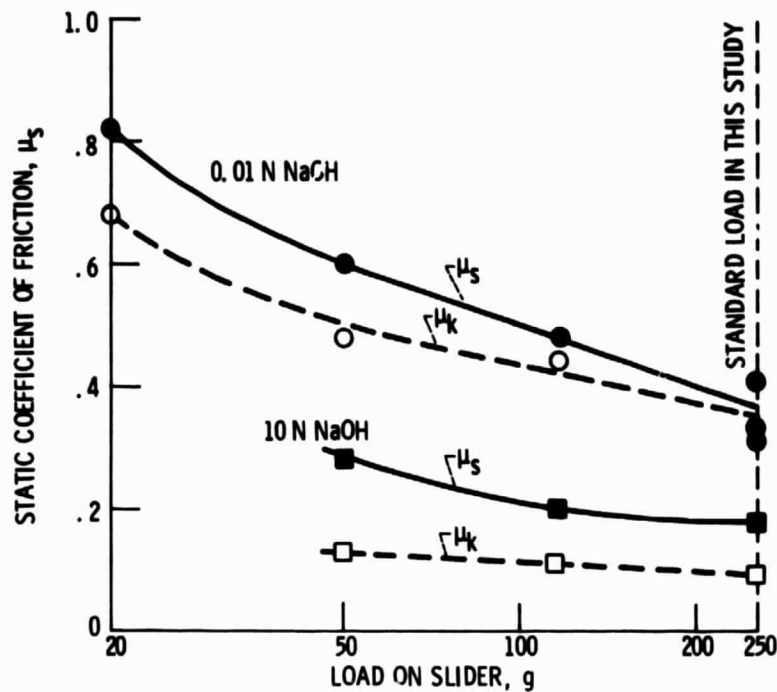


Figure 7. - Effect of normal load on coefficient of friction. Iron in NaOH at 0.01 and 10N, saturated with air.

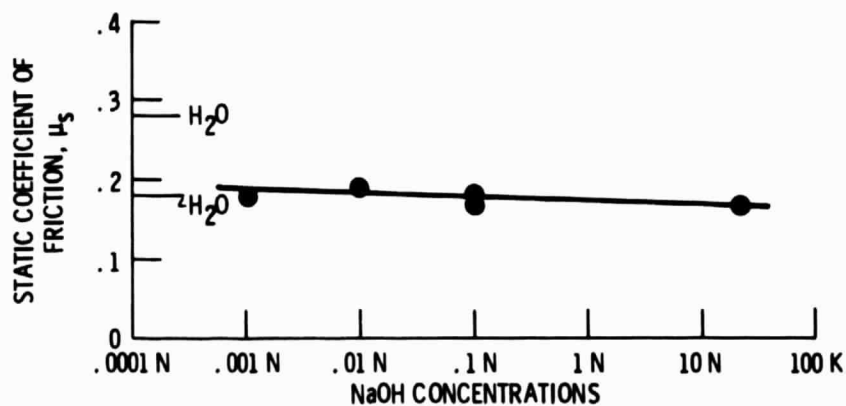
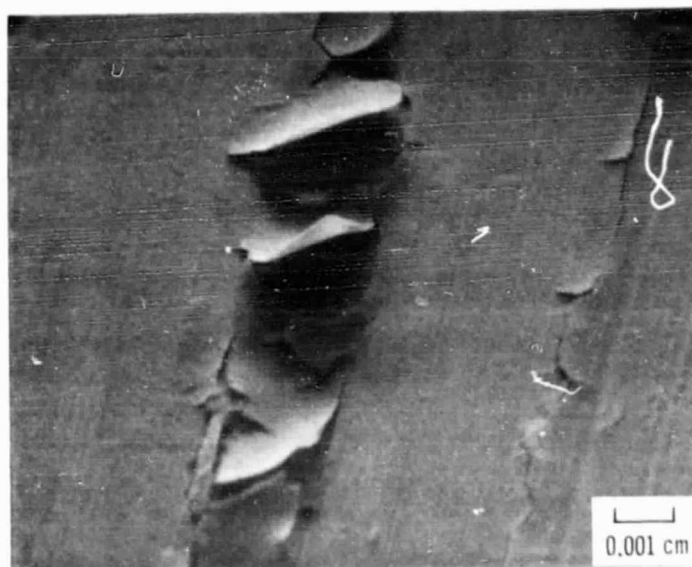
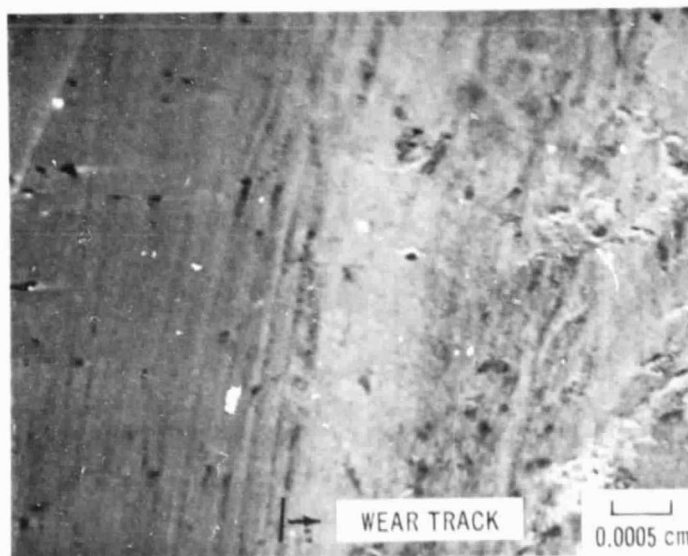


Figure 8. - Effect of water and of NaOH concentration on static coefficient for Al_2O_3 ball sliding on nickel flat in NaOH solutions.

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(a) H_2O
 $\mu_s = 0.28$



(b) 0.1 N NaOH
 $\mu_s = 0.17$

Figure 9. - SEM photographs of wear tracks made with water and with 0.1 N NaOH on nickel.

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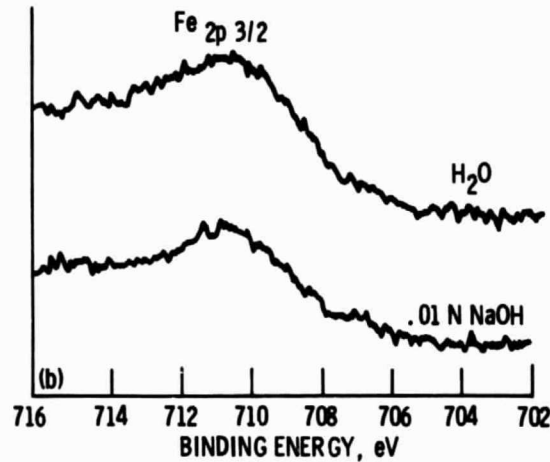
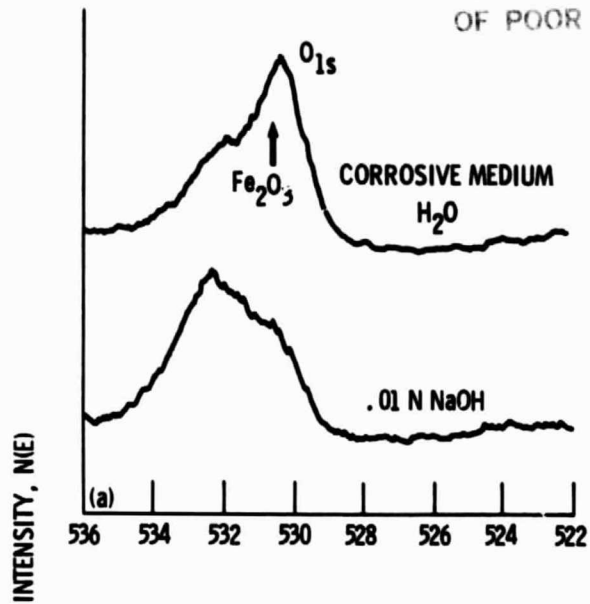


Figure 10. - XPS data on wear surface of iron.

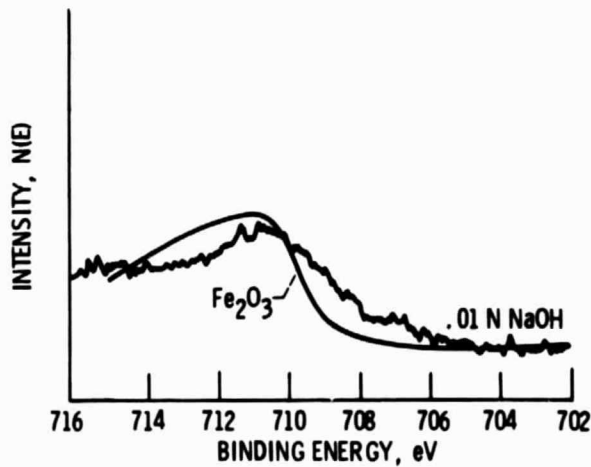
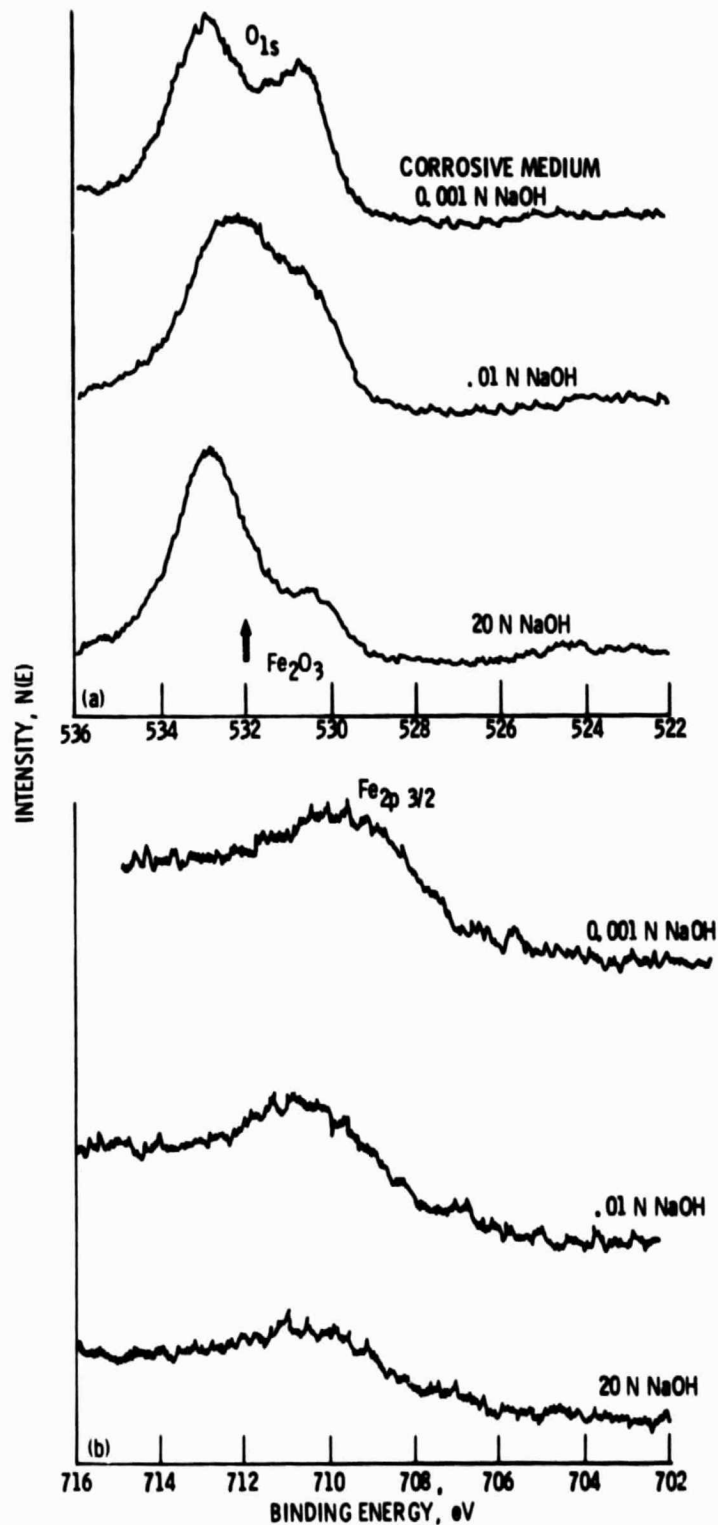


Figure 11. - Standard XPS energy curve for Fe_2O_3 according to reference 11, compared with the curve obtained for iron under 0.01 N NaOH.

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(a) Oxygen 1s binding energy.

(b) Iron 2p 3/2 binding energy - 716 to 702 eV.

Figure 12. - XPS data of wear surface of Iron Indicating effect of sodium hydroxide normality on water surface chemistry.