

Experimental Study of Chemical De-scaling-I: Effect of Acid Concentration

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Abstract

Chemical cleaning is employed frequently for de-scaling exchangers in combination with other cleaning methods. A customized chemical solution is circulated through the scaled apparatus for certain time following drainage and washing. Many cycles of cleaning may be necessary to reach satisfactory de-scaling level. The composition of the cleaning liquor is very important for efficient de-scaling. The scale from an industrial boiler is treated with four different acid solutions at five different strengths to study their dissolving effect on the scale/deposits in the tubes of the boilers. Results reveal that 5% solution of HCl is the most effective to dissolve the scale in a specified time at room temperature. Sulfuric acid shows very poor de-scaling properties under the test conditions. The order of effectiveness to dissolve the scale deposits is HCL > HNO₃ > HCOOH > H₂SO₄. Hydrochloric acid may provide 30-50% savings on the circulation time as compared to HNO₃ based on the rate of dissolution.

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Introduction

The internal surfaces of a water tube boiler are in contact with water to produce steam. Water used for steam generation inevitably contains dissolved solids due to inefficient water purification processes. Some salts (e.g. Calcium salts) decrease solubility at higher temperature and hence deposit (scale) on the exchanger surface. The scale & deposits in boiler tubes are generally nonmetallic and therefore possess low thermal conductivity, which impedes transfer of heat and thereby affects the efficiency of the boiler. Periodic cleaning of the exchangers is mandatory for an optimal thermal efficiency. Various methods for de-scaling are available and are used standalone or in combinations. Chemical cleaning is frequently employed for cleaning complex exchanger surfaces. Since the scale compositions vary depending on many factors, a solution has to be customized for specific applications [1] [2].

The deposition of solids within boilers under steaming conditions results in an accumulation of sludge or in the production of scale. The deposits in the form of scale are highly objectionable, since they are poor conductors of heat, cause reduced efficiency, and are often responsible for burned tubes or plates. The mechanism of scale formation is complex and has been for many years the subject of much controversial discussion. The scale resulting from the deposition of mineral constituents in boilers often consists not of a single salt but of a number of compounds combined in forms frequently unlike the salts originally present in the feed water this is the natural consequence of physical and chemical phenomena resulting from the reactions at high temperatures and pressures existing in steam boilers. Much material has been published relating to fuel losses from scale. Many of the early investigators results are misleading, however, since their conclusions were based upon insufficient and unreliable data. The heat-insulating properties of scale may not be measured in terms of thickness only [1].

Water-side scale build-up in boilers is a progressive, inevitable process. Even with stringent control of feed water and condensate chemistry, scale and deposition will occur. The main problems caused by boiler scales are (a) Increase in tube wall temperature; hence, boiler tube ruptures, and (b) decrease in overall boiler efficiency, hence, increase in energy cost and loss of reliability. The increase in tube wall temperature is a result of the low thermal conductivity of scales as compared to the metal. The reduction in heat-transfer could lead to the design temperature of the tube wall being exceeded, which in turn might lead to the failure of the tube by creep rupture.

The scale of various compositions on the heat transfer surfaces may be recognized as:

- Corrosion products such as iron and copper oxides,
- Alkaline scale Ca(OH)_2 and MgO ,
- Additive scales consisting of calcium and magnesium combined with additive materials that are usually soft and easily removed, and
- Calcium Sulphate.

For calcium sulphate scale there is as yet no widely accepted chemical cleaning process and mechanical methods are usually adopted [3].

Overall efficiency for a boiler may be defined as the ratio of steam output to the fuel consumption. Again, since scaling impedes heat transfer, more fuel is required to produce a given amount of steam, thus reducing overall efficiency and loss of energy. Eventually, removal of scale from the boiler becomes essential if damage to the boiler is to be prevented. One way of removing scale is

to chemically clean the boiler. Chemical cleaning is a multiple stage process that seeks to remove all the existing scale from the boiler internals, leaving a clean, passivated waterside system. One step in the process involves the use of inhibited acid to dissolve the scales. This acid stage is potentially damaging to the boiler and therefore, it requires careful monitoring to prevent serious metal loss.

A case study of de-scaling brine heaters using chemical methods is reported in [4]. Chemical methods using sodium glycollate, EDTA and sodium carbonate solution/dilute inhibited hydrochloric acid were employed in the laboratory to dissolve the scale. Alternate reaction with sodium carbonate solution and inhibited hydrochloric acid was chosen for in - plant de-scaling process. The method was found successful in removing most of the scale after three cycles of chemical cleaning.

The successful development and application of chemical de-scaling method involves kinetic study of the reaction of the scale with the cleaning liquor (acid). Acid is usually inhibited to prevent corrosion of the base metal [5] [6].

This article presents an experimental study of dissolution of the scale obtained from an industrial water tube boiler in different acid solutions at varying strengths. The results are presented and discussed.

Brief Chemistry of Boiler Scales

The primary constituent of boiler scale is; Magnitide which is formed as a result of reaction of metallic iron with high temperature steam. Other crystalline materials, shown in table 1 may also form the scales. Copper is present due to corrosion of copper alloy, aluminum bronze feed water condensers and pre-heaters, often because of oxygen entrance into these systems. Copper is transported through the steam cycle where it forms on the boiler internals. Other constituents shown in Table 1, are transported through the steam cycle and deposited on boiler internals either from contaminants contained in the boiler feed water system or from use of outdated phosphate-based water treatment chemicals. In addition to these crystalline inorganic compounds, there may be organic residuals present in the scale [1].

Table 1: Compounds generally found in water boiler scales (source is [1])

Compound	Formula
Anhydrite	CaSO ₄
Aragonite	CaCO ₃
Brucite	Mg(OH) ₂
Copper	Cu
Calcite	CaCO ₃
Hematite	Fe ₂ O ₃
Hydroxyapatite	Ca ₁₀ (OH) ₂ (PO ₄) ₆
Magnetite	Fe ₃ O ₄
Quartz	SiO ₂
Thenardite	Na ₂ SO ₄
Wollastonite	βCaSiO ₃

Advantages of chemical de-scaling of heat exchangers

As for as mechanical cleaning is concerned there are brushes and pigs used for cleaning process, which can only clean the parts of the equipment that are not of complex shape such as the tubes of boiler and pipes. Some heat exchangers are of complex shape that's why they cannot be mechanically cleaned. So for this purpose chemical cleaning is used.

Experimental

The scale deposit was collected from the tubes of an Industrial water tube boiler from Manzoor Sizing & Textile Industries Faisalabad. The scale samples were prepared and treated chemically in the laboratory of NFC-IEFR Faisalabad. Standard methods for the preparation and testing of different acid solutions were adopted. For each test run 5g of scale was added in to a fixed volume of acid solution in a flask. The contents were kept for an hour at room temperature without agitation. The residue was filtered, dried, and weighed.

Results and Discussion

The test conditions and the weight loss of the scale for various acids at different strengths are given in Tables 2-5. Effect of Nitric acid is presented in Table 2, which show a steady increase in dissolved mass of the scale with acid concentration. Thus higher acid concentration results in faster de-scaling.

Table 2: Effect of concentration of HNO₃ (Nitric Acid) on weight loss of the sample

Concentration	Time	Initial weight scale	Final weight of scale	Dissolved scale
	min.	g	g	g
1%	60	5	4	1
2%	60	5	3.6	1.4
3%	60	5	2.1	2.9
4%	60	5	1.7	3.2
5%	60	5	0.9	4.1

The loss of weight of the scale versus concentration of HCl is given in Table 3. The loss in weight is increasing. It is also observed that at equal acid concentrations the weight loss is higher with HCl. Therefore, HCl is superior on dissolving the test scale over HNO₃.

Table 3: Effect of concentration of Hydrochloric Acid (HCl) on weight loss of the sample

Concentration	Time	Initial weight scale	Final weight of scale	Dissolved scale
	min.	g	g	g
1%	60	5	3	2
2%	60	5	2.5	2.5
3%	60	5	1.4	3.4
4%	60	5	1	4
5%	60	5	0.3	4.7

While Nitric acid and Hydrochloric Acids are efficient on dissolving the scale, Sulfuric acid shows poor solubility of the scale. The scale is not dissolved below 3% acid concentration. At higher concentration only 0.5g is dissolved in one hour. It is not an appropriate choice for de-scaling, results indicate.

An organic acid (Formic acid), along with inorganic acids (HNO_3 , HCL, and H_2SO_4), is also employed for de-scaling tests. The mass of dissolved scale increases with concentration and then decreases. This shows that there exists an optimum concentration of formic acid which will produce maximum de-scaling rate at the test conditions. The scale is more soluble in Formic acid than Sulfuric acid. The loss of mass of scale is summarized in Table 6.

Table 4: Effect of concentration of Sulfuric acid (H_2SO_4) on weight loss of the sample

Concentration	Time	Initial weight scale	Final weight of scale	Dissolved scale
	min.	g	g	g
1%	60	5	5	0
2%	60	5	5	0
3%	60	5	4.5	0.5
4%	60	5	4.5	0.5
5%	60	5	5	0.5

Table 5: Effect of concentration of Formic acid (HCOOH) on weight loss of the sample

Concentration	Time	Initial weight scale	Final weight of scale	Dissolved scale
	min.	g	g	g
1%	60	5	4	1
2%	60	5	4	1
3%	60	5	3.5	1.5
4%	60	5	3	2
5%	60	5	2.7	1.3

Table 6: Dissolved mass of scale in different acid solutions for 5g sample in 60 minutes

Concentration	Time	Dissolved Scale in			
		HCl	H ₂ SO ₄	HCOOH	HNO ₃
%	min	g/5g sample			
1	60	2	0	1	1
2	60	2.5	0	1	1.4
3	60	3.4	0.5	1.5	2.9
4	60	4	0.5	2.	3.2
5	60	4.7	0.5	2.3	4.1

Given the loss of scale in the acid solution as m_{loss} , the mass of the sample as m_{sample} , and the time of dissolution as t , percent dissolution (D) of the scale can be computed from Eq. 1.

$$D = \frac{m_{loss}}{m_{sample}} \cdot 100 \quad (1)$$

The percent loss versus acid concentration is shown in Figure 1 for four acids. It is evident that solubility of the scale is increasing with concentration for HCl and HNO₃. Solubility increases from 40% to 94% and 20% to 80% over concentration of 1-5% for HCl and HNO₃ respectively. Solubility in Formic acid is 20% in 1% acid solution, which increases to 40% at 4% concentration and then decreases to 30% at 5% concentration. A maximum is found at 4% with Formic acid. The scale is insoluble in H₂SO₄ solution at 1% and 2% concentrations. In 3% and higher concentration solutions, the solubility remains at 10% only.

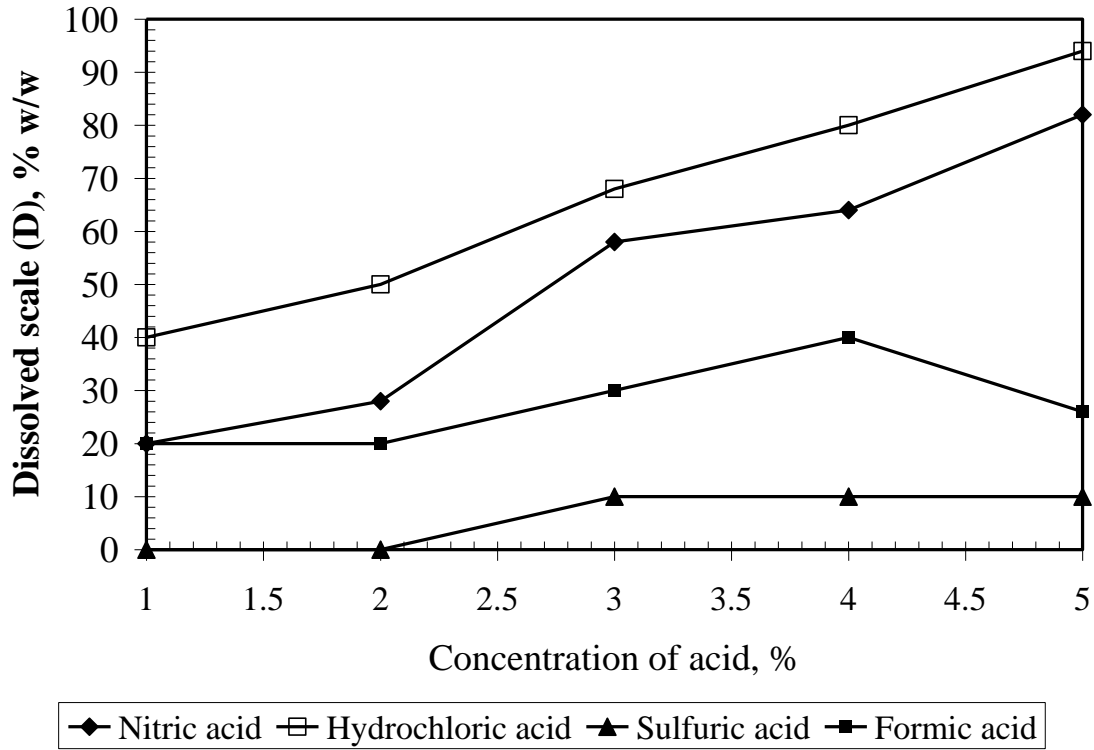


Figure 1: Percentage of dissolved scale versus acid concentration

Average specific rate of de-scaling (R) is calculated from Eq. 2.

$$R = \frac{m_{loss}}{m_{sample} \cdot t} \quad (2)$$

The rate of dissolution of the scale in various acid solutions is depicted in Figure 2. The rate is increasing for HCL and HNO₃ with concentration. The rate increases from 0.0066 to 0.015 g/g-min and from 0.0035 to 0.013 g/g-min for HCl and HNO₃ respectively over 1% to 5% acid concentration. The data shows a maximum rate of dissolution at 4% concentration of Formic acid. The rate is zero at and below 2% H₂SO₄ concentration and 0.0018 g/g-min after 3% concentration. It is observed further that the rate of dissolution in HNO₃ and HCOOH are equal at 1% concentration. However the rate of dissolution in HNO₃ at higher concentration is many folds. The trends of the curves indicate that the difference in average rate of dissolution in HCl and HNO₃ decreases with increasing concentration, however, data at higher concentration is not available to make an unequivocal statement.

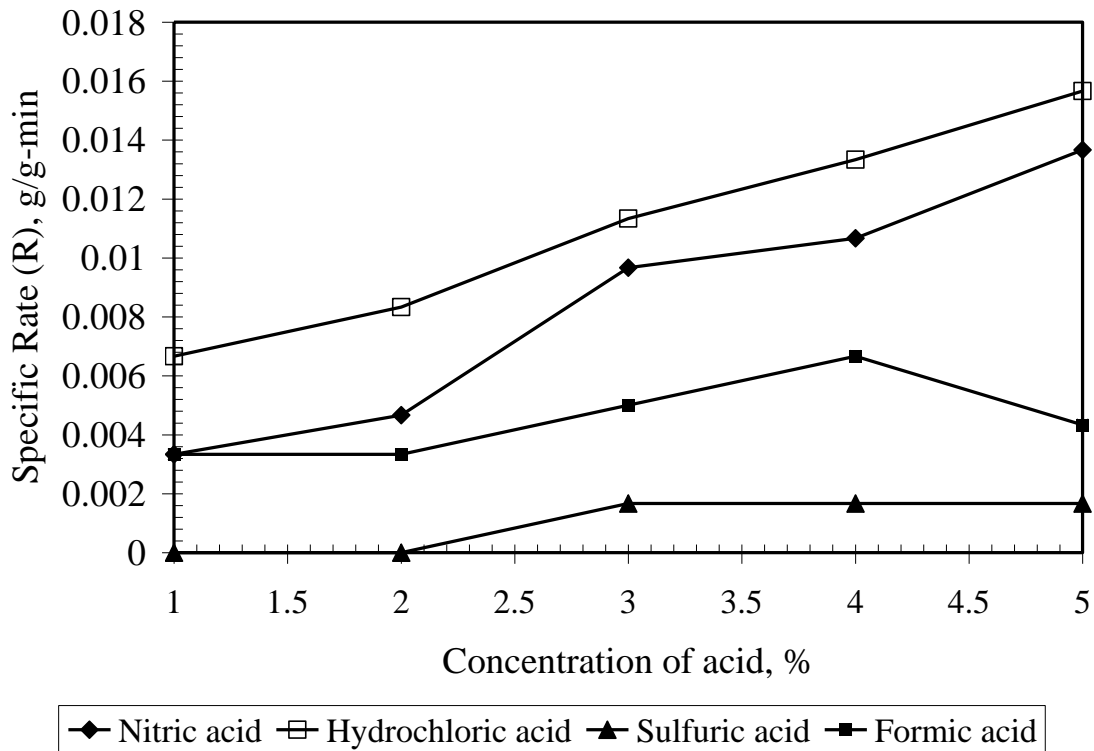


Figure 2: Rate of scale dissolution versus acid concentration

From these results one can say that HCl and HNO₃ are better candidates to be used for chemical de-scaling of the exchanger tubes. HCl may provide 30-50% saving on circulation time as compared to HNO₃ based on rate of dissolution.

Conclusion

Chemical cleaning is frequently employed for cleaning complex exchanger surfaces. Since the scale compositions vary depending on many factors, a solution has to be customized for specific applications.

The experiments are performed on the scale obtained from an industrial water tube boiler. Fixed amount of scale sample is allowed to stand in fixed volume of acid solution for fixed time interval. Mass which is dissolved by the acid solution is determined gravimetrically. Experiments are repeated with four acids at five concentration levels.

From experimental results with different acids (organic/inorganic) one concludes that Inorganic acids work more efficiently than organic acids. It is evident that hydrochloric acid works the most efficiently. Since the solubility of the scale is increasing with concentration, higher concentration of HCl seems beneficial for de-scaling if corrosion problem does not involve. It is reported, however, that high concentration of acid will cause corrosion to the metal surface so 5% is an optimum. Sulfuric acid reacts very slowly with the scale deposit while comparing with the organic acids. The order of effectiveness to dissolve the scale deposits is HCL > HNO₃ > HCOOH > H₂SO₄. Hydrochloric acid may provide 30-50% saving on circulation time as compared to HNO₃ based on rate of dissolution.

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