

# An Experimental Study on Degreasing of Zircaloy Tubes and Optimization of Process Parameters

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## Citation

Pankaj Kumar Battabyal, Debapriya Mandal. An Experimental Study on Degreasing of Zircaloy Tubes and Optimization of Process Parameters. *International Journal of Modern Physics and Application*. Vol. 6, No. 1, 2019, pp. 1-8.

**Received:** December 10, 2018; **Accepted:** May 16, 2019; **Published:** May 30, 2019

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**Abstract:** In the reducing operation of zircaloy tubes, lubricants are applied on both inner and outer surfaces, which must be cleaned before vacuum annealing of the tubes. Degreasing is a vital unit operation in production of zircaloy tubes, which are used as cladding of fuels for nuclear power plants. The rate limiting operation of the multistage degreasing of zircaloy tubes is the treatment with hot alkali solution. Different lubricating oils have been used in the tube reducing mill. A detailed study was felt necessary, since it is the rate determining step in the degreasing operation. In this operation five different chemicals are used sequentially for saponification, chelation, emulsification, deflocculating and wetting. Selection of proper physico-chemical parameters may reduce the soaking time. The effect of the concentration of different chemicals and process parameters on the cleansing action was studied with an objective to find a cost effective optimum composition for degreasing operation. The detailed process of degreasing, parametric study, results, optimization of process parameters and conclusions are discussed in this paper.

**Keywords:** Zircaloy, Degreasing, Nuclear, Fuel Tubes, Power Plants, Cleansing Solution, Alkaline

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## 1. Introduction

Zirconium (Zr) is a precious metal in the nuclear industry. Its unique properties *viz.*, high mechanical strength, low neutron absorption cross section and high corrosion resistance enables it to be used for fuel cladding, pressure and calandria tubes and other reactivity control mechanisms in nuclear reactor components [1]. Greases used in the greasing operations are generally, toxic [2]. Lubricating oils are used in all tube reducing operations like pilgering, in which a layer lubricating oil of is provided to lubricate the moving surfaces of machines, reduce the heat generation, and minimize frictional loss and to hinder surface wear under extreme temperature and pressure conditions. These materials are generally a mixture of various hydrocarbons, modified with various thickeners and other additives to impart the required characteristics for specific applications [2]. Persistent solvents are used to remove greases and lubricants from various machine elements in the washing processes. Proper removal of these products from the metal

parts, tubes etc. after use is necessary for the continuous and repetitive operation of machinery processes. In fact, not easy to remove greases and lubricating oils from the tubes as they are complex mixtures designed to resist degradation during strenuous use. The degreasing efficiency is dependent on the physical characteristics and chemical composition of grease.

Till date, the treatment processes to degrease zircaloy tubes have not been studied in details. In the present study, the development of an alkaline degreasing method that employs a specially prepared batch of chemicals was explored. It was found that the important parameters in alkaline degreasing baths are chemical concentration, treating time, temperature and total alkalinity. Moreover, hardness of the water also effects degreasing operation. Experiments were carried out with various different compositions of chemicals under varying operating conditions. The degreasing efficiency of the new alkali bath treatment was evaluated by visual, water drop test and cotton swipe tests. The cost effectiveness of the process was also investigated in this study. The results of this study are expected to

demonstrate the general applicability of the alkaline degreasing system. The present study and knowledge of the technical know-how of the degreasing process will enable all the indigenous degreasing industries to have a correct degreasing solution at a much lowered cost and with greater efficiency. Moreover, the study will also enable us to degrease and develop solution that can be used to degrease more stringent greases and solutions that are most frequently used in leather and automobile industries.

## 2. Materials

In the present work, commercial grade sodium hydroxide was used. Commercial Sodium Gluconate was procured from Global Calcium Private Limited, India. Sodium Meta-Silicate of Neeta Chemicals Private Limited, India was used. Tri-sodium phosphate of Indian Rare Earths Limited, India was used. Mono-ethylene Glycol was procured from Impex Chemical Corporation, India. Distilled water was used to carry out the experimental work.

The main component present in the lubricating oil is chlorinated paraffin. Paraffin wax is a white or colourless soft solid derivable from petroleum, coal or oil shale that consists of a mixture of hydrocarbon molecules containing between eight and forty carbon atoms. It is solid at room

temperature and begins to melt at about 37 °C. Its boiling point is >370 °C [3]. The chlorinated paraffin can react with alkali metals and alkaline earth metals which have a strong affinity for chlorine. They can react with iron, zinc and aluminium at high temperatures leading to decomposition. In fact that alkali degreasing method is the best possible method in order to remove the greasy materials from the surface of the tubes [4-5]. Table 1 shows the composition of different lubricants; used in metal forming processes.



Figure 1. Schematic diagram of the experimental setup.

Table 1. Composition of different lubricants; used in metal forming processes.

Sr. No.	Composition	% Composition of lubricating agent
1.	C14-17 chlorinated paraffin	50 - 100
2.	Distillates (petroleum), solvent de-waxed heavy paraffinic	1 - 5
3.	Distillates (petroleum), hydro-treated heavy paraffinic	1 - 5

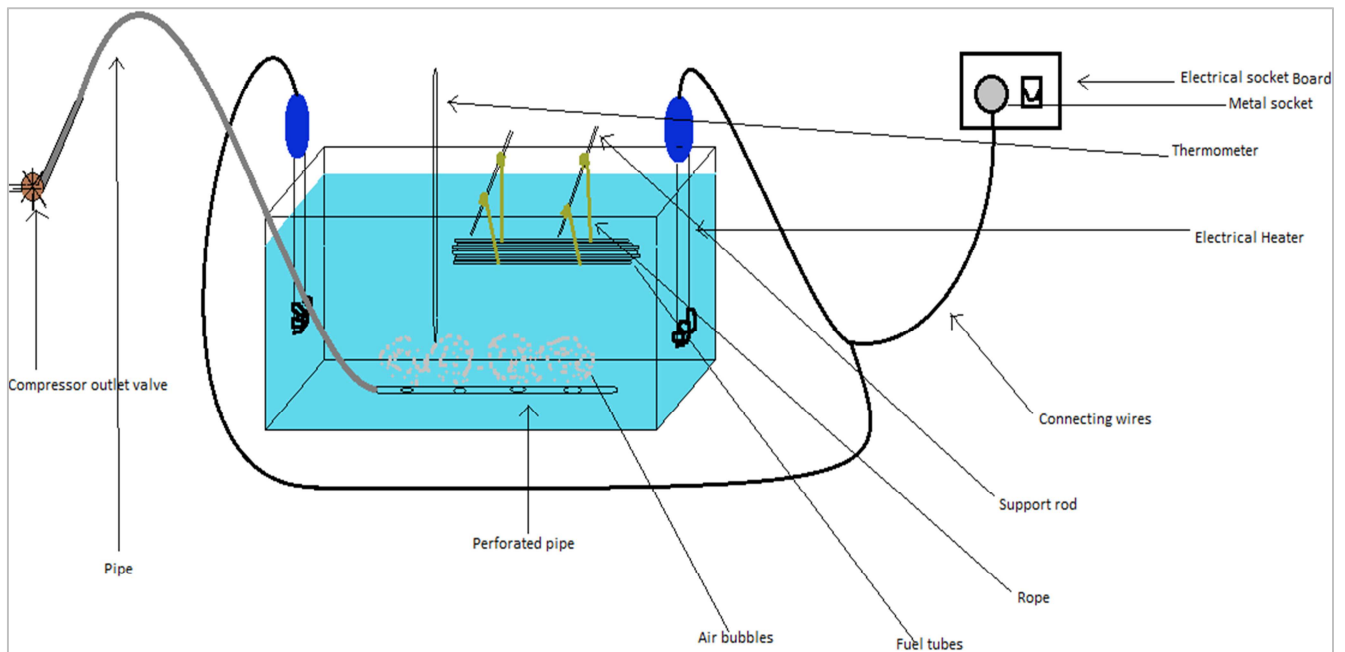


Figure 2. Experimental tank for preparation of alkali bath.

### 3. Experimental Setup

The degreasing operation was carried out in a specially prepared alkali bath. The bath was prepared in a SS-304L tank mounted with heaters so that the temp can be varied accordingly while conducting the experiments. To maintain the temperature at a particular value, a thermocouple was connected to constantly monitor the bath temperature. In addition to this, a compressed air supply with a control valve was connected to the bottom of the tank with nozzles at varied intervals to agitate the bath. All the chemicals were added accordingly which include sodium hydroxide, mono-ethylene glycol, sodium meta-silicate, tri-sodium phosphate and sodium gluconate and thereafter mixed with distilled water to create the desired bath composition. Some greased fuel tubes were taken which would be required for studying the properties of the alkali bath on the cleansing action of the tubes. Figure 1 shows the schematic diagram of the experimental setup. A stainless steel -304L tank was taken keeping in mind, the high alkalinity of the solution. The volume of the tank was 166 litres. The alkali bath of volume approximately 140 litres, as shown in Figure 2 was prepared using a perfect combination of chemical composition.

### 4. Methodology

The chemical composition was varied after each set of experimental observations were noted down. A bunch of scrap tubes of zircaloy tubes were taken and they were dipped in grease. As the alkali bath temperature reading showed 79°C, the greased tubes were dipped in the alkali bath. The start of the soaking time was noted down. The batches of tubes were allowed to soak in the alkali bath for varied interval of time. The first lot of tubes was removed at an interval of one h and its soaking time was noted down. In this way the second batch of tubes were removed at the completion of second h and so on. The tubes were then checked to know the efficiency of their grease removal. Initially a visual inspection is done. In the second step a fresh white cotton rag is swiped over the entire length of the tube. In the third and final step the water drop test is carried out. If the water skids down without forming small droplets, the tube is declared fit for vacuum annealing and sent for further mechanical operations. The removal efficiency or % Cleanliness of the tubes was calculated to quantify the

amount of grease removed.

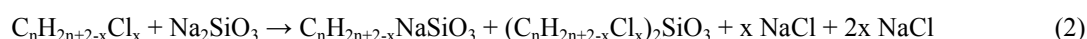
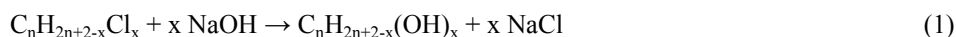
### 5. Results & Discussions

It was found from experiments that the increase in concentration of de flocculating agent reduces the dependency on imported sodium gluconate. It was also observed that pneumatic agitation compensated the role of tri-sodium phosphate and hence the usage of chemicals used in preparing the alkali bath was reduced to 4 h. Increasing the concentration of sodium hydroxide increased the pH of the solution and this facilitated in reduction of the soaking time from 5 h initially to one h in the final. It was also found that the soaking time can be greatly reduced the temperature of the bath maintained constantly at 75-80°C. Pneumatic agitation was tried and this was found to be quite successful in maintaining a homogeneous composition through the bath and keeping the greasy materials away from the tubes i.e. the role played by the emulsifying agent or buffer solution. Further cost analysis of the chemicals used was carried out and it was found that the new composition is economically viable and the same composition can be carried out on a commercial scale for the degreasing of the tubes.

A study of the effect of the disposal of the various chemicals on the environment, human beings and aquatic animals was carried out and found that none of the three chemicals used in the preparation of the new alkali bath is harmful for the ecosystem in any manner. A quantitative method of knowing when the bath is to be disposed was found using various analyses. It was found that appreciable differences in free NaOH content, pH and density was observed between the fresh and disposed samples. But, only mild differences in viscosity and conductivity were observed between the two solutions.

#### 5.1. Reactions

Reaction between chlorinated paraffin with sodium hydroxide, acting as saponifying agent present in the alkali bath to form sodium chloride that get deposited at the bottom in the form of salt and an organic compound (Reaction 1). Reaction between chlorinated paraffin with sodium meta-silicate that act as a deflocculating agent present in the alkali bath to form corresponding organic sodium silicates and sodium chloride as salt that get deposited at the bottom in the form of salt (Reaction 2).



In Reaction 2, n varies from 14 to 17 and x varies from 1 to 7.

The deflocculating agent by virtue of forming silicates tend to keep all the paraffinic compounds apart from each other and hence tend to provide a steric repulsion between two adjacent organic silicates. The introduction of these functional groups interacts with the particle surface by charge

compensation. Here the positively charged "anchor" group of the additive attaches itself to negatively charged silicates. Since the polymer chains of the additive contain functional groups with positive and negative charge, there are controlled attractive and repulsive effects. Hence, there is a targeted compensation of agglomeration tendencies.

## 5.2. Effect of Temperature

The reaction between ethyl acetate and sodium hydroxide to give sodium acetate and isopropyl alcohol is an example of a saponification reaction. The rate expression consists of rate constant which is the temperature dependent term. From heat balance calculations, the activation energy of the Reaction 1 was found to be 39.91 KJ, which means it is an example of exothermic reaction. Thus, as we increase the temperature the rate constant increases and hence, the reaction rate also increases. Figure 3 shows the change of soaking time and rate of evaporation with bath temperature. It was found that,

up to 77°C as the temperature increases, rate of evaporation increases slowly, beyond this rate of evaporation increases steeply. Since, with increase in temperature evaporation loss of water increases, this increases the concentration of chemicals in the solution. Due to this, degreasing efficiency decreases since only a batch with a particular concentration of chemicals will aid cleansing action. The loss of water also affects the density of the solution as a result, the equilibrium between attractive and repulsive forces in the water-solids-deflocculant-system is changed and, hence, the viscosity of the bath.

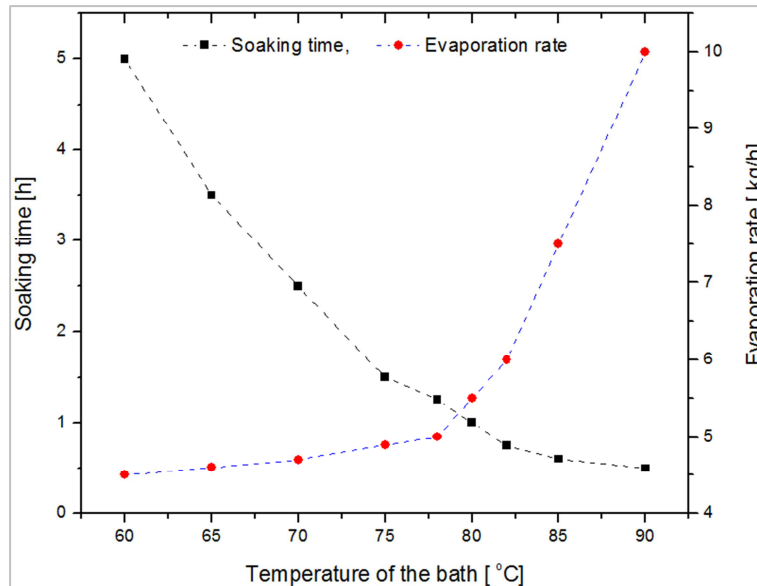


Figure 3. Change of soaking time and rate of evaporation with bath temperature.

## 5.3. Effects of Chelating & De-Flocculating Agent

Increase in concentration of sodium meta-silicate which acts as a de-flocculating agent reduces the dependency on sodium gluconate, which acted as a chelating agent. Chelating agents are used in detergent formulations because they inactivate the hardness arising out of minerals like calcium and magnesium, and reduce undesirable effects of other dissolved metals such as iron and manganese. Chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. While a deflocculating agent prevents fine soil particles or clay particles in suspension from coalescing to form flocs [6-7]. So, initially the greases were accumulated by chelation effect and later on these same accumulated complexes were kept apart by de-flocculation effect. Therefore the greases can be kept apart separately just by increasing the concentration of the deflocculating agent and not allowing the greases to accumulate.

But there is a particular limit up to which the de-flocculation agent can be added because Unsuitable de-flocculant content can lead to superimposition of the zeta potentials, thus preventing maximum repulsion of neighbouring particles. The consequence can be undesired agglomeration. Two raw material particles with a diffuse layer which do not mutually influence

each other, on account of a low density, the distance between them is so large that the zeta potentials do not overlap. If the density is greater, there is superimposition of the zeta potentials of neighbouring raw material particles [8-10].

When an optimum electrolyte concentration prevails in the bath, the zeta potentials of the neighbouring particles set up an ideal equilibrium between the attractive and repulsive forces. This leads to optimum repulsion between the particles. If more than the optimal quantity of deflocculant is added, the diffuse layer becomes thinner with increasing electrolyte concentration [8-10]. At too high electrolyte concentrations the attractive forces predominate once again, the agglomeration tendency increases because the diffuse layers are too thin. Due to the smaller distances between the particles of raw material, the agglomeration tendency of slips increases with increase in density.

## 5.4. Effect of Saponifying Agent

Sodium hydroxide acts as a Saponifying agent and its main function is involved with the cleansing action of the greasy materials from the surface of the tubes [5]. Increasing the concentration of NaOH greatly aids in cleansing action but an increase after a certain extent, it suppresses the role played by the de-flocculating agent and hence the cleansing quality comes down.

### 5.5. Effect of Emulsifying Agent

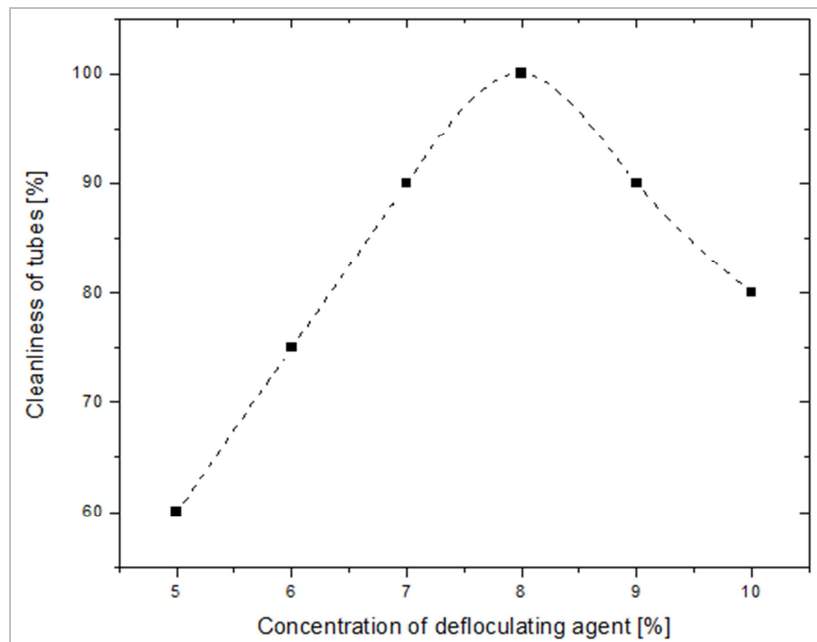
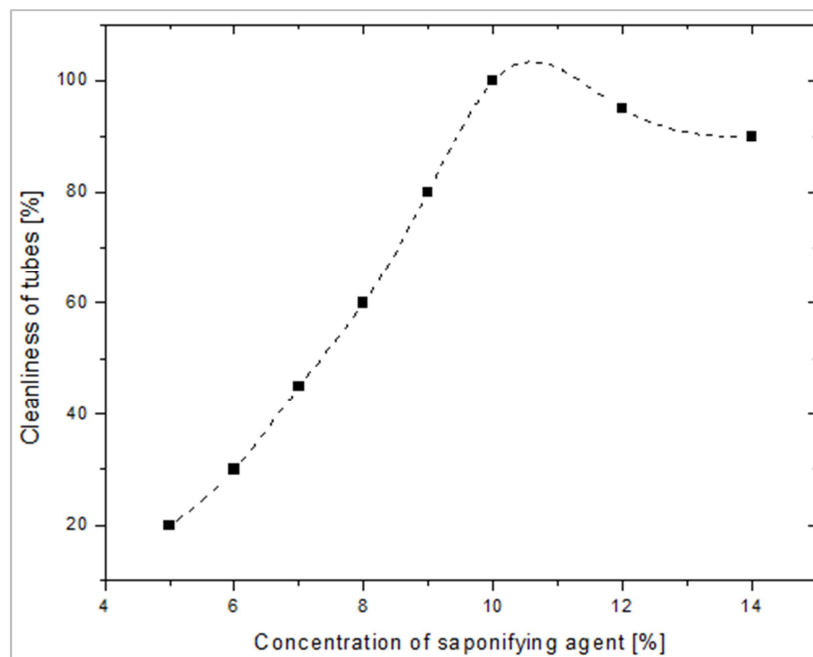


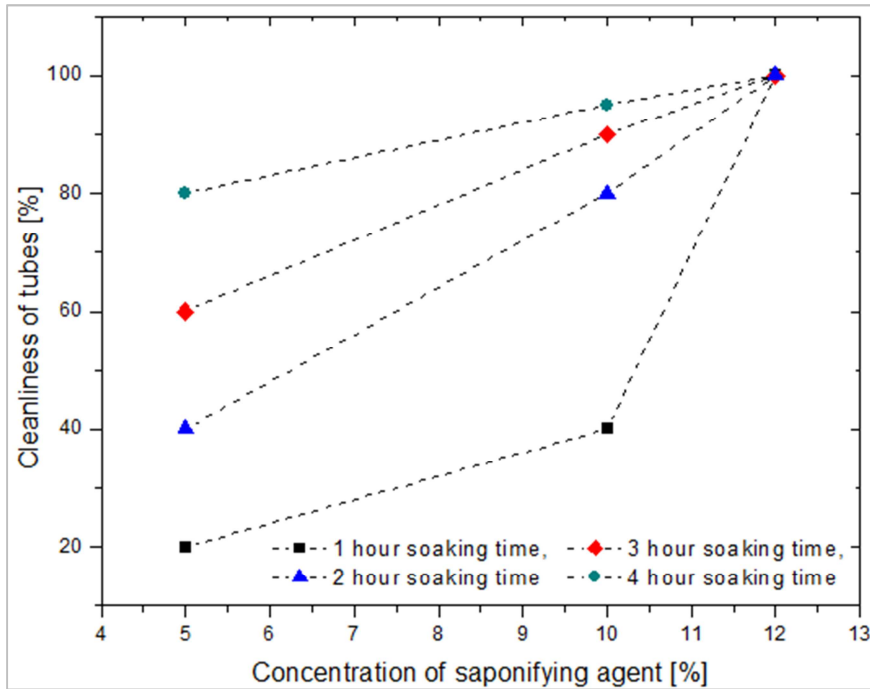
Figure 4. Change of the cleanliness with concentration of de-flocculating agent.

Tri-sodium phosphate acts as an emulsifying agent. Emulsions are stabilized by adding an emulsifier or emulsifying agents. All emulsifying agents concentrate at and are adsorbed onto the oil-water interface to provide a protective barrier around the dispersed droplets. In addition to this protective barrier, emulsifiers stabilize the emulsion by reducing the interfacial tension of the system [6]. Figure 4 shows the change of the percent cleanliness with the concentration of de-flocculating agent. The change in cleanliness with change in the concentration of saponifying agent for constant soaking time of 1 h is shown in Figure 5

(a) and the same with varying soaking time is shown in Figure 5(b). Usage of tri-sodium phosphate posed some threat to environment, hence a pneumatic agitation facility was incorporated and this acted well as there was no change in cleanliness quality as shown in the graph below. Figure 6 shows how the cleanliness of tubes changes with the concentration of emulsifying agent. It was found that up to 5% the cleanliness of the tubes increases, beyond this no further improvement in cleanliness of the tubes was observed.



(a)



(b)

Figure 5. Change in cleanliness with change in concentration of saponifying agent, (a) for constant soaking time of 1 hour and (b) with varying soaking time.

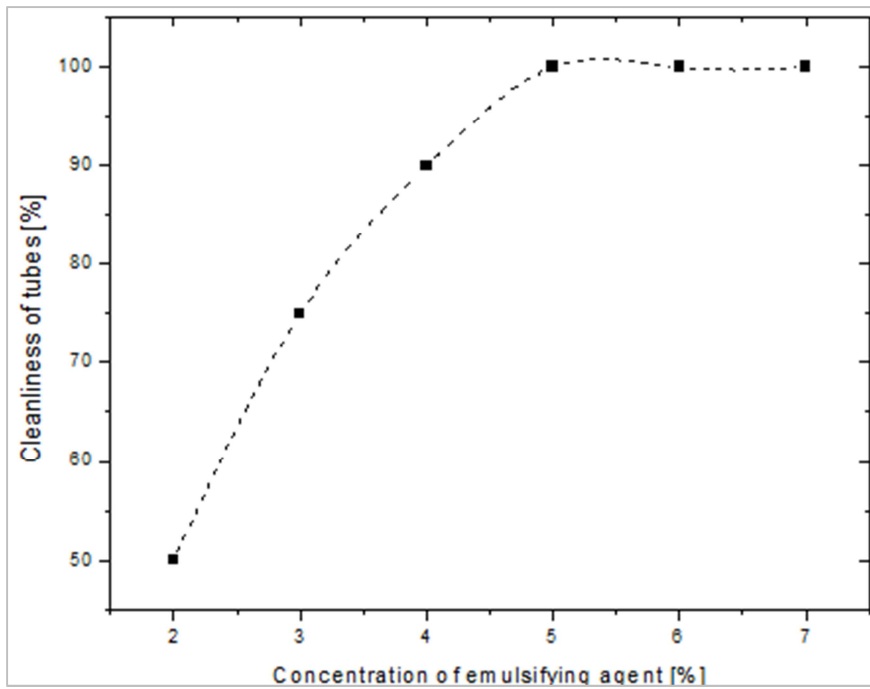


Figure 6. Change in cleanliness with change in concentration of emulsifying agent.

The air agitation always kept the emulsions on the top of the bath which can be easily skimmed off. It was found that, with increase in air pressure, the cleanliness of tubes increases until the air pressure increases up to 6 bar as shown in Figure 7. It was also found that, when the air pressure increases more than 6 bar the cleanliness of the decreases.

This may be due to the effect of pressure on the cleansing effect of different chemicals viz., mono-ethylene glycol, sodium meta-silicate, tri-sodium phosphate and sodium gluconate. Thus, 6 bar is the optimum air pressure at which degreasing operation may be carried out.

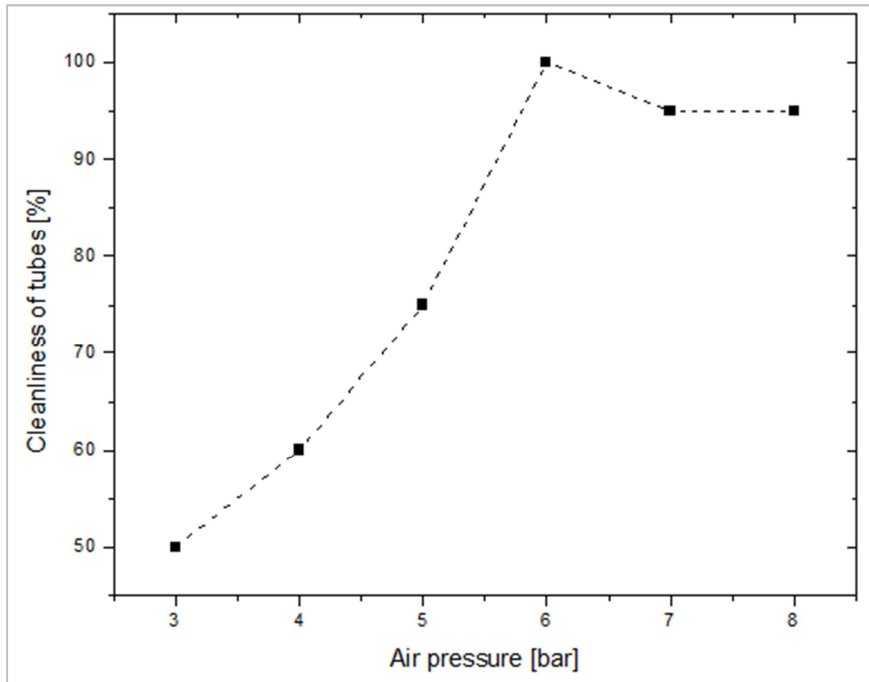


Figure 7. Change in cleanliness of tubes with increase in air pressure.

## 6. Cost Analysis

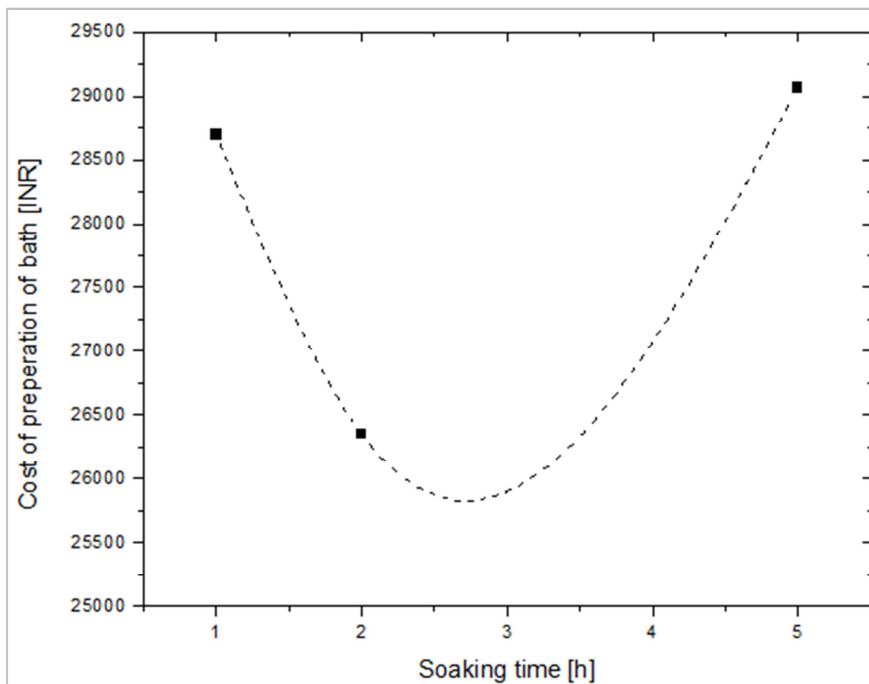


Figure 8. Variation in cost (in, INR: Indian Rupees, ) with soaking time.

The soaking time was reduced to an h from 5 h initially. A new composition of chemicals were tested on an experimental scale to reduce the soaking time considerably but in order to use it on a commercial scale the same composition of chemicals need to be economically viable. The soaking time has been reduced keeping the cost of the preparing the alkali bath almost constant. Figure 8 shows the variation of the cost of the preparation of bath with soaking

time. It was observed that soaking time of 2.5 to 3 h is the optimum and this was due to the removal of costly sodium gluconate and increasing the concentration of caustic soda pellets.

## 7. Conclusions

It was first observed that pneumatic agitation compensated



the role of tri-sodium phosphate while an increase in concentration of sodium meta-silicate (from 5 to 8%) nullified the requirement of (imported) sodium gluconate. Further, as the alkaline concentration was increased, soaking time reduced from 5 h initially to 1 h with 10% NaOH concentration. It was also observed that aqueous dissolution of caustic soda is exothermic reaction and the temperature of the bath rose to 51.5°C. Pneumatic agitation facilitated the bath homogenization & cooling and ensured complete dissolution. The minimum soaking time that ensures complete cleaning of the greased fuel tubes were determined followed by visual testing; cotton rinsing and water drop tests.

Chemical analysis was carried out on fresh and depleted bath samples and differences in properties like free NaOH content, pH, density, conductivity and density were noted. This led to quantification of bath life, i.e. when pH falls from 13 to 10.7 and the free NaOH content of the bath decreases from 9.10% to 3.95%, bath may be disposed. Appreciable difference in conductivity was not found which suggests lack of ionic content in the lubricating oil. Also it was found that the cost of the new bath is cheaper compared to the earlier w. r. t chemical & electrical costs. Hence, the experimental bath may be scaled up to commercial / regular production use.

## Acknowledgements

The authors acknowledge the support from the Department of Atomic Energy, Government of India for providing funds and resources to carry out this study.

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## Biography



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