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Study on Acidity Control of Fire-Resistant Control Fluid [FRF] Fuller's Earth Vs. Strong Base Resin an Comparative Performance

Vani G. D, Pranay, A. K. Das
NTPC Limited

***Abstract*:- Turbine governing system of thermal power plant, with unit size 500 MW or more, uses phosphate ester-basedfire-resistant control fluids (FRF) to ensure safety against fire hazards. The fluid is pressurized, subjected to elevated temperatures at control valve surfaces, flows through fine clearances and is exposed to contaminants including water, dirt, and air during its play within governing system. It causes degradation of EHC fluid. Maintenance of such oil is of utmost important as moisture ingress from control valve steam end damages the working molecules aggressively through hydrolysis to produce acidity in oil that can otherwise be prevented to a great extent. Moreover, FRF is more than 10 times costlier at present time due to less competitive purchase option. High temperature effect causes thermal degradation (pyrolysis) of oil to generate fine carbon particles, that make the oil black colored. Corrosion, valve sticking, and other unsatisfactory system performance may result when such phosphate esters are deprived of proper fluid maintenance.**

Various techniques are available in market to address the aforesaid oil deterioration related concernsie., re-conditioning to reduce the acidity level in used / degraded FRF, as well as removal of finely dispersed carbon particles in oil to improve functioning and aesthetic look of oil. Present study focuses on comparative ability of acidity removal from FRF by conventional fuller's earth material and dried strong base anion resin. Study shows that SBA resin removes acidity more efficiently than fuller's earth material and TAN level can be lowered even to 0.05 mg KOH/gm of Oil from an initial valueas high as 0.5-1.0. Removal of high moisture content (>1000 mg/kg) from FRF down to 400 mg/kg isalso achievable through application of high vacuum (0.08 Torr; 30-minute duration) to sprayed oil chamber or through other techniques.

However, EHC fluid purification is not limited to acidity control. It is also important to keep the fluid clean and dry if it is to operate efficiently and offer a long service life. Mechanical techniques are therefore needed to complement and maintain the activity of the resin treatment. For example, resin fouling by particulate can reduce its activity and this may require improved filtration.

Key words: Fire resistant control fluid, Tri-xylenyl phosphate / TXP, Hydrolysis, Pyrolysis, Fuller's earth, Total acid number / TAN, Strong base anion resin]

INTRODUCTION:

Fire resistant hydraulic fluid is used as a control fluid for units 500 MW & above, particularly to address the issue of higher fire hazard. This is a phosphate ester based synthetic fluid, with special properties and designed for long service life. The fluid should remain free from mineral oil contamination to retain its special properties.

Reliable and economical power generation in an eco-friendly manner is of paramount importance and a major challenge to electrical power producers to meet the energy demand of near future. Present generation installations are aiming primarily with super critical and ultra- super critical technologies and even exploring feasibility of advanced USC technique that are expected to exceed the plant efficiency
>45%, along with reduction on CO_2 emission level compared to conventional sub-critical units. With increasing steam temperature & pressure (540 → 600 →710°C; 180 →247 → 280 →310 kg/cm^2) at turbine end, fire hazard from lubrication system also increases, due to which mineral oil becomes unsuitable for high temperature application to governing system of turbine also. Fire resistant phosphate ester-based control fluid becomes the priority choice for governing system of gas turbine, large capacity steam turbine and in nuclear power plants (600-1000MW). The burning profile of mineral oil and differentsynthetic fluids that are used as lubricant cum coolant is shown below (figure1).

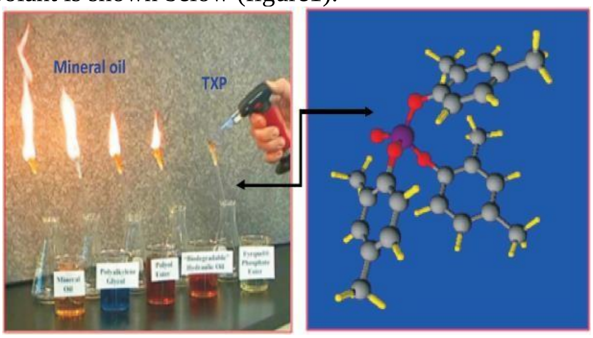

Figure 1. TXP and its burning profile

In general, properly maintained fluid can run for 15 years or more with conventional conditioning/purification arrangements provided. Average temperature faced by FRF in governing system is although <70°C, but faced valve surface temperature is high. High temperature and high moisture in control fluid are the two main factors responsible for fluid degradation. The operative processes behind fluid degradation are (i) hydrolysis and (ii) thermal degradation (pyrolysis).

Hydrolysis of FRF results acidity development by phenol derivatives and phosphoric acid and this process also contributes color to oil. Acids so produced attacks cylinder / actuators to causecorrosion & ceasing of control valve.

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Maintenance of FRF:

Conventional FRF conditioning system uses fuller's earth material for acidity removal and molecular sieve to remove moisture content in oil. Oil conditioning is done through circulationof a part of fluid (2-5%) through kidney loop arrangement. Disadvantage of earth material is that (i) it produces soapy material duringacidity neutralization processand finally results foaming tendency at a Ca / Mg level of 35-40 ppm in oil (ii) contributes fine particles of earth material to oil that deteriorates NAS levelbeyond 7 / increases ISO contamination code beyond 15/12 and that can interfere in smooth operation control valve and charring of oil on valve surface (iii) responsible for air entrapmentin oil and air release value increases beyond 5 minute.

On the other hand, molecular sieve performs in a slow manner to remove moisture from oil. It requires regeneration in correct interval by heating at >250°C and monitoring for its desired performance (<500 ppm moisture at outlet of cartridge). In case of performance with lesser efficiency, moisture level in FRF is remains at 800-1100 ppm level that promotes hydrolysis of fluid to produce more acid. Under such situation, overall acidity level gradually increases, although fuller's earth cartridge is functional (acid formation rate > acid scavenging rate by fuller's earth). It is seen that the factors like, water, air, metal contamination and heat that are responsible for fluid degradation, are often not managed in existing fluid conditioning system.

Examination And Maintenance Aspects <u>Fluid Properties:</u>

There are many designs (types) of hydraulic equipment each of which subjects the fluid to conditions which affect its performance and properties. The most stringent conditions exist in equipment operating at high pressure (up to approximately 140 bar) and very close clearances in micron level.

The properties which have the greatest influence on equipment design and operation are:

- Viscosity
- Density
- Thermal and oxidation stability
- Air release
- Foaming
- Resistivity (corrosion-erosion)
- Cleanliness For equipment subject towater ingress:
- Hydrolytic Stability
- Demulsibility

Phosphate ester fluids are particularly susceptible to thermal and hydrolytic degradation and to a lesser extent to oxidation. Temperature and water are, therefore, of particular importance in all types of equipment and must be controlled.

Parameters Requiring MonitoringAcidity

i) Causes of Increase

a) Degradation of fluid due to increase in moisture content or high fluid temperatures.

b) Chemical contamination of system

c) Ineffective operation of Fullers Earth filters where these are fitted.

ii) Harmful Effects

Acidity may cause corrosion or equipment malfunction if allowed to persist, particularly in the presence of moisture.

Latest Technology for Acidity reduction in FRF:

To eliminate the disadvantages of fuller's earth treatment in acidity reduction of phosphate ester-based control fluid, earthmaterial is getting replaced by air dried strong base anion resin. Treatment with SBA resin not only reduces acidity of FRF but also removes metal ions (Ca/Mg) from fluid that helps in controlling foaming. The ion exchangeprocess introduces some moisture in fluid and requires strong moisture removal technque likevacuum treatment of oil, dry nitrogen capping / continuous purging, etc.

Purification Treatment

The principal behind all conditioning systems is that the rate of acid removal must be greater than the rate of production. If not, the control of the fluid degradation is lost, the acidity will increase quickly, andfluid life will be considerably shortened. However, purification is not just about the removal of acid but also about keeping the fluid dry and clean.

Resin Composition and Structure

Chemically, ion exchange resins are based on a divinylbenzene or polystyrene core onto which different functional groups can be introduced. These functional groups can react with other chemicals leading either to an exchange of ions or to the adsorption of the chemical onto the resin surface. As a result, unlike Fuller's Earth or Selexsorb, they can remove different degradation products or contaminants from solution. Function of commercially available resin types is described in Table 1

TABLE **1 : Function of Commercially Available Resin Types**

Resin Type	Benefits	Disadvantages
Weak Base Anion	Removes strong acids and metal soaps/salts byadsorption	Weak acids remain
Strong Base Anion	Removes weak acids	Strong acids remain
Weak Acid Cationic	Will remove neutral soaps	Releases acid into he fluidLess thermally stable Large volumechanges on goingfrom H^+ to M^+ form
Strong Acid Cationic	Will split neutral soap	Releases acid into solution. Need to use chloride-free version of resin
Chelating	Remove acid rapidly	May release sodium into the fluid with possible adverse effect on soap precipitation and foaming properties.

EXPERIMENTAL:

Total acid number (TAN) analysis was doneat different cycles as per ASTM D974 using standard alkali solution. Stanhope-seta make oil conductivity meter was employed for electrical resistivity/ conductivity monitoring of fluid as per ASTM D2624.

Figure-2: Tests in progress with fuller'searth & SBA resin

New fuller's earth material from NTPC plant and Lewatit mono plus MP 800 resin (SBA / TEC:
1.0 meq/ml) was used for lab study to compare acidity (TAN) reduction rate / efficiency. 05 gm of fuller's earth (bed height: 7.5 cm; bed volume:7.5 ml) & 05 gm of SBA resin (regenerated & hot air dried; bed height: 7.0cm; bed volume: 7.0ml) were used for performance (TAN reduction) comparison up to 12 cycles. Resin drying was done at 60-80°C using hot air for 15 minutes.50 ml of Control fluid (FRF with TAN: 0.49 mg KOH/gm of fluid; Moisture: 1170 ppm) was passed at a flow rate of 4.0 ml/minute in each case (figure-2). Elemental analysis (Ca, Mg) was carried as per ASTM D6595 using RDE- OES technique & MOA-II plus equipment.

RESULTS & DISCUSSION:

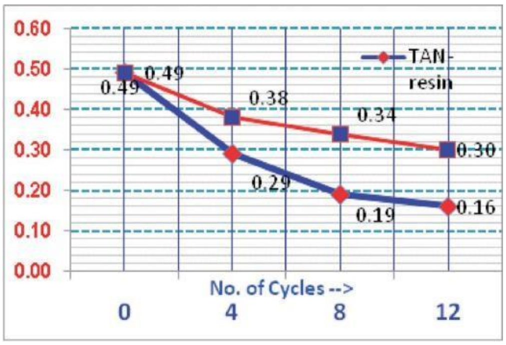

Figure-3: TAN reduction: fuller's earthVs.Resin

On the other hand, when FRF was treated with same quantity of SBA resin, a sharp drop in TAN value was observed at a rate of 0.05 TAN/ cycle and then up to 12th cycle drop rate was
0.01 TAN/cycle (figure 3). Thus, overall rateof change of TAN found to be 0.03TAN/cycle. After 6th cycle of treatment, resin appears to be exhausted. To know the possible extent of TAN reduction, experiment was carried with double quantity of resin and it showed that, within 10th cycle, acidity drops below 0.1 mg/gm oil and after 25th cycle TAN value reaches to 0.04. This indicates that so long exchange capacity of resin remains, sharp drop in TAN takes place @ 0.04 TAN/cycle. Therefore, enough of SBA resin to be present in vessel / cartridge to remove acidity of FRF to <0.05 TAN within 10cycles. 1 ml of FRF with 0.5 TAN may require 0.6-0.7ml SBA resin for the same.

Resistivity / Conductivity variation:

During cycling of FRF through fuller's earth, fluid conductivity varies as: 2620 →1650 pS/ cm at 25ºC in 12 cycles and hence a minor improvement in resistivity also takes place (0.38 →0.61 Gohm-cm). As reaction of acids / substituted phenols with fuller's earth producessoap / salt, conductivity don't drop below 1000 pS/cm. In case of SBA resin, conductivity of fluid varies as: 2620 →350-550 pS/cm after 12 cycles. Resistivity improves from 0.38 to 1.81 / 2.85 Gohm-cm after 12 cycles, depending on residual effective resin.

Table-2: Variation of TAN & resistivity usingvolume ratio of FRF & SBA resin (1:0.6):

CYCL E NO.	TAN (mg KOH/ gm)	Con-ductiv-ity pS/cm	Resis-tivity (Gohm-cm)	Residual leached ele-ments	
				Ca (ppm)	Mg (ppm)
0	0.49	2650	0.38	35	42
10	0.08	355	2.82	9	3
20	0.05	275	3.68	7	2
25	0.04	272	3.70	5	1

Moisture content in such resin treated fluid changes from 1170 ppm to 1250 ppm, which on high vacuum treatment for 30 minutes reaches to 450-500 ppm moisture with improvement in resistivity value also (>7 Gohm-cm)

Leached element variation:

During fuller's earth treatment, Ca content do not vary much cycle to cycle but Mg content becomes half. In case of SBA resin treatment, both Ca & Mg content goes below 10 ppm after10th cycle as shown in figure-4 below.

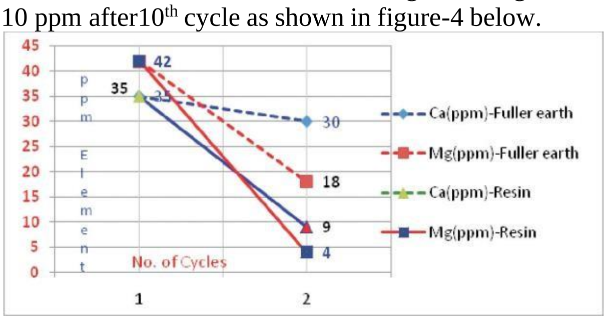

Figure-4: Variation of Ca & Mg level duringFuller's earth & Resin treatment

Table- 3: Comparative data on residualleached element in FRF on treatment:

Cycle No.	Treatment with Fuller's earth			Treatment with SBA resin		
	Ca (ppm)	Mg (ppm)	Resistivity	Ca (ppm)	Mg (ppm)	Resistivity
0	35	42	0.38	35	42	0.38
10	30	18	0.58	9	4	2.8

CONCLUSION & RECOMMENDATION:

- In case of steam turbine, where steam ingress into fluid is a common phenomenon and temperature effect causes hydrolysis of phosphate-based control fluid faster to generate acidity from phenol derivatives, a robust & fast mechanism to eliminate organic acidity is very much essential for good health of governing system.
- Dried strong base anion resin with exchange capacity of 1.0 eq/l is highly effective to remove acidity from FRF (0.5-1.0 TAN) at a rate of 0.05 TAN/cycle, when FRF: SBAresin (ml/ml) is 1: 0.7 or better.
- Acidity removal rate per cycle by SBAresin is almost twice the rate by fuller's earth material. Moreover, it is capable to manage high acidity without any deterioration of other properties (foaming problem, drop onresistivity of oil, etc.).
- SBA resin treatment of FRF improves resistivity to desired level (>5 Gohm- cm at 25ºC) if moisture controlling be done effectively. Only SBA resin or Mixed resin treatment (SBA + a little SAC) or use of commercially available ion charge bonding (ICB) cartridge technology is able to control both TAN and earlier leached fuller's earth elements (Ca / Mg) or soap material from FRF, thereby improving resistivity, anti- foamingcharacter and good air release value (<7minute) also.

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REFERENCES:

[1] William David Phillips et.al., *"Ion Exchange* Habermas, R.E., Howard, L.R. and LaVere, D.J., *"In-service reconditioning of turbine generator hydraulic fluid",* Power Engineering, 54-5, March, 1982. *Phosphate Ester FluidsUsed in Steam-Turbine Control Systems"* ; Feb-2016. *Mechanical Purification of Fire-Resistant*

[2] Phillips WD & Sutton DI, *"Improved Maintenance and Life extension of Phosphate Esters using Ion-Exchange Treatment",* Journal of Synthetic Lubrication, 13, 3, 225-261, 1996

[3] Ken Brown; *"Managing the health of Fire resistant Steam turbine Electro- hydraulic control oils",* Machinery Lubrication,May-2001.

[4] Technical bulletin and MSDS of Reolube 46XC from Kemture Corporation, USA.

[5] *Staniewski JWG, "Maintenance Practices for Steam Turbine Control Fire resistant Fluids",* Part-1, Journal of Synthetic Lubrication, 23, 3, pp- 109-121, 2006.

[6] Staniewski JWG, *"Maintenance Practices for Steam Turbine Control Fire resistant Fluids",* Part-2, Journal of Synthetic Lubrication, 23, 3, 123- 135, 2006.

AUTHORS:

	Anil Kumar Das; B Tech., M Tech.(Electrical), MBA (Operation Management), ASNT Level-3 qualification in Ultrasonic Testing, Magnetic Testing, Electromagnetic Testing & Penetrant Testing. ASNT Level 2 qualification in Visual & Radiographic Testing. He has 30 years of work experience in the field of health, life assessment including latest and reliable NDE methods for power plant components. Presently working as GM (NETRA).
	**Pranay M.Sc. (Chem.), M.Tech** has 16 years of work experience in field of ash utilization, biomass & coal combustion, commissioning and operation of D.M. Plant, Coal and Combustion of thermal power plants. He is having various research publications in International & National journals and various papers presented in International and National conferences/seminars/workshops.
	**Vani G.D M.Sc.Engg** by Research has 11 years of work experience in the field of Oil Tribology, Air preheaters, bowl mills and Rotary parts of power plant machineries, Sophisticated Instrumental analysis andConditioning assessment of Lubricating oil analysis. Presently working as Manager (NETRA)