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## SUPPORT ON WATER CHEMISTRY AND PROCESSES FOR NUCLEAR POWER PLANT AUXILIARY SYSTEMS

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### INTRODUCTION

The Argentine Republic is currently running two nuclear power plants: Atucha I (C.N.A. I, a PHWVR) and Embalse (C.N.E., a PHWR) operated by Nucleoeléctrica Argentina (N.A.S.A.) whereas the Argentine Atomic Energy Commission (C.N.E.A.), among other activities, is responsible for research and development in the nuclear field, operates research reactors and carries out projects related to them. In particular, the Reactor Chemistry Section personnel (currently part of the Chemistry Dept.) has been working on the field of reactor water chemistry for more than 25 years, on research and support to the N.P.P.s chemistry department<sup>1</sup>. Though the most relevant tasks have been connected to primary and secondary circuits chemistry, ancilliary systems show along the time unexpected problems or feasible improvements originated in the undergoig operating time as well as in phenomena not foreseen by the constructors.

These reasons alone justify the existence of a local group who should have abundant sources of information, good knowledge of the local suppliers market, engineering capability and access to modern analytical techniques, without disregarding consults to the designers.

In particular PHWRs have a system devoted to the purification and upgrading of the collected heavy water leaks. The purification train is fed with different degradation ratios ( $D_2O/H_2O$ ), activities and impurities.

The water is distilled in a packed bed column filled with a mesh type packing. The mesh wire is made of a bronze substrate covered by copper oxides whose current composition has been determined by Mossbauer spectroscopy.

With the purpose of minimizing the column stack corrosion, the water is pre-treated in a train consisting of an activated charcoal bed-strong cationic-anionic resin and a final polishing mixed bed resin. Ionic chemicals like acetic acid (whose provenance is suspected to come from the air treatment/ $D_2O$  recovery system where the regeneration is performed at high temperature) are detected by the conductivity and ion chromatography when they concentrate at the column bottom.

Traces of oils are retained by the charcoal bed but some compounds extracted by the aqueous phase are suspected to be responsible for the resins fouling or precursors of potentially aggressive agents inside the distillation column. Those species have been detected and identified by gaseous chromatography-mass spectrometry (GC-MS).

In the present work, the identification, evaluation of alternatives for the retention and results compared to the original products present in the water upgrading purification train have been summarized.

### DESCRIPTION OF THE SYSTEM AND DETECTED ANOMALIES

In a PHWVR the heavy water ( $D_2O$ ) leaks that come from the primary heat transport system (PHTS) or the moderator system (MS) have to be collected, clasified in accordance to their provenance, relative activity and degradation (with  $H_2O$ ). Thus, the station designers have previewed a  $D_2O$  upgrading system (HWUS) attached to the auxilliary systems of the plant. Also, the air treatment system collects  $D_2O$  from the environment and is periodically regenerated. The product, mixtures of  $H_2O-D_2O$ , contributes to the HWUS inlet material. Other<sub>1</sub>

sources of water could be pumps sealing devices or lubrication devices such as the ones located in the refuelling machine. Decontamination chemicals (organic acids) and cleaning products could be present either. Then, the inlet product composition could not be well predicted although it is inscribed in a relatively known range of compounds.

In regard to the HWUS itself, it is composed by a set of collecting tanks, an activated carbon bed, a cationic and anionic resin beds and a polishing bed, after which the water is stored in a product tank. This product is routinely analyzed and has to be maintained in a tight range of specifications: pH, conductivity and organics present in the input and output locations of each of the components of the system. Organics are followed by total organic carbon (TOC) measurements, GC-MS and ion chromatography. The water specifications<sup>2</sup> are presented in Table 1.

pH	6.5 - 8
Conductivity ( $\mu\text{S} / \text{cm}$ )	< 3
oil (ppm)	< 1
organics (ppm)	< 10
Gd (ppm)	< 1
B (ppm)	< 1

From the product tank the water is fed into a rectification column. The column is a packed bed type distillation device which has a bronze based mesh covered by copper oxides<sup>3</sup>. The Mössbauer spectra of the surface is shown in Figure 1.

A signal of non-proper behaviour of the purification train has been the presence of acetic acid in the product water and later in the HWUS column bottom, with a possible increase in the corrosion rate of the packing mesh, which in turn is followed by the Cu concentration in the latter location.

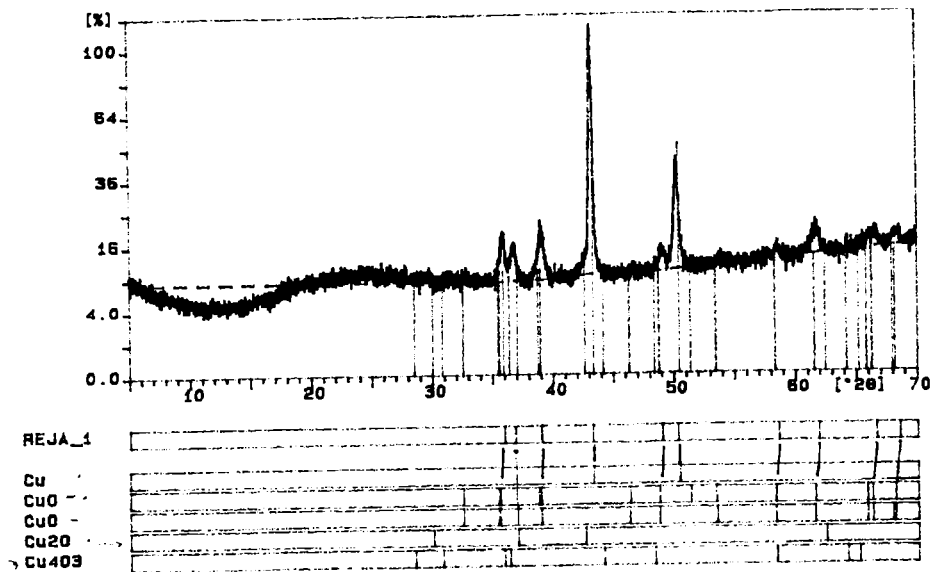


Figure 1: Mössbauer spectra of the packed bed column mesh.

## METHODOLOGY AND COMPOUNDS DETECTION RESULTS

With the purpose of presenting quick and cost-feasible solutions to the problem of the presence of acetic acid in the HWUS column bottom it has been carried out a survey of the possible organic sources (ionic and non-ionic) in the installation as well as a literature review.

The revision of the problem in other plants<sup>4,7</sup> has shown that in one case a powerful UV-H<sub>2</sub>O<sub>2</sub> equipment<sup>5,6</sup> was installed immediately after the product water tank while in other case a second activated carbon bed was placed in that point. Both operators claim that the problem has been overcome.

With the aim of detecting the origin of the acetic acid and other organics, samples have been taken from different points of the installation and the conclusions have been as follows:

(i) It has been found acetic acid in the regeneration devices of the enclosures air treatment system, which has been designed also to collect traces of D<sub>2</sub>O and for this reason addresses its effluents to the HWUS.

(ii) After some operating hours, the acetic acid concentration rises in the column bottom and can be detected by ion chromatography as well as by a rather slow pH decrement and conductivity increase.

(iii) Samples of the product tank, when analyzed with a GC-MS equipment and a total organic carbon equipment have shown the presence of acetic acid in a concentration lower than 2 ppm and 7 ppm of TOC. It has to be remarked though, that the polishing mixed bed was close to its breakthrough point. On the other hand, traces of oil whose commercial denomination is LifeGuard 90 or Turbina 46 have been detected in the same sample. It has been speculated that the possible source of this oil is the refuelling machine.

From the evidences, world previous experience and present study sampling, it has been concluded that the acetic acid, non-detected in the normal operation of the purification train but undergoing concentration in the HWUS column, could be responsible for the pH reduction and Cu concentration increment. Besides, the traces of organics that are not-retained by the activated carbon could produce fouling on the resin beds anticipating their breakthrough or diffculting their proper species retention.

## PRELIMINARY STUDIES

Table 2 presents the main characteristics of the oil employed in the refuelling machine<sup>8</sup>. In the circuit, the oil is contacted with the water with the subsequent transference of organics. With the purpose of identification of these compounds, it has been contacted oil with water (ratio 1:3), the water filtered through black stripe grade filter paper (Whatman 41, 25 µm) and a GC-MS spectra determined, which is shown in Figure 2.

**Table 2:** LifeGuard 90 oil characteristics

Test	ASTM	Turbine EP 46
viscosity (40 °C), CSt	D-445	44
viscosity (100 °C), CSt	D-445	6.4
viscosity index	D-2270	95
flash point (°C)	D-92	205
drain point (°C)	D-97	-9
acid number (mg KOH/g)	D-974	0.2
oxidation establiity (hs)	D-943	> 2000
air stripping	D-3427	5

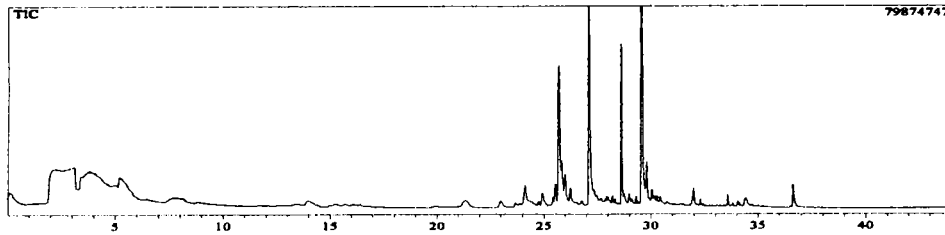
With the aim of testing separation processes, emulsions of oil-water have been filtered through 25 and 0.45 µm filter paper. On the filtered samples has been measured TOC and new GC-MS spectra have been performed. The TOC concentration along with the filtrated volume are presented in Figure 3.

## SELECTION OF RETENTION AGENTS

The filtration curves have shown the presence of organic matter in the filtrate, that is, the oil is not retained in the filters and the extraction experiment shows that some compounds go to the aqueous phase. From these points it has been inferred that the organics could foul the purification train and enter into the HWUC, while they also could hinder the retention of weak acids.

It has been then carried out a market survey with the goal of selecting an alternative for the activated carbon and the resins. The product especifications<sup>9,10</sup> are presented in Tables 3 and 4.

aceite lifeguard 90  
 \*\*\* CLASS-5000 \*\*\* Report No. = 1 Date : ACEITE.D01 01/05/15 15:58:59  
 Sample : aceite lifeguard90  
 ID :  
 Sample Amount : 1  
 Dilution Factor : 1  
 Type : Unknown  
 Operator : oless  
 Method File Name : ACEITE.MET  
 Vial No. : 1  
 Barcode :



**Cromatograma efectuado por purga y trampa sobre el extracto acuoso del aceite**  
**(A/O = 3,5)**

**Se identifican:**

**2- hexanol  
 xilenos  
 benzaldehido  
 heptanol  
 heoctanol  
 2-etilhexanol  
 octenal**

**Se observa la presencia de otros compuestos cuya identificación no es concluyente.**

Figure 2: GC-MS spectra of the laboratory extracted and filtered sample.

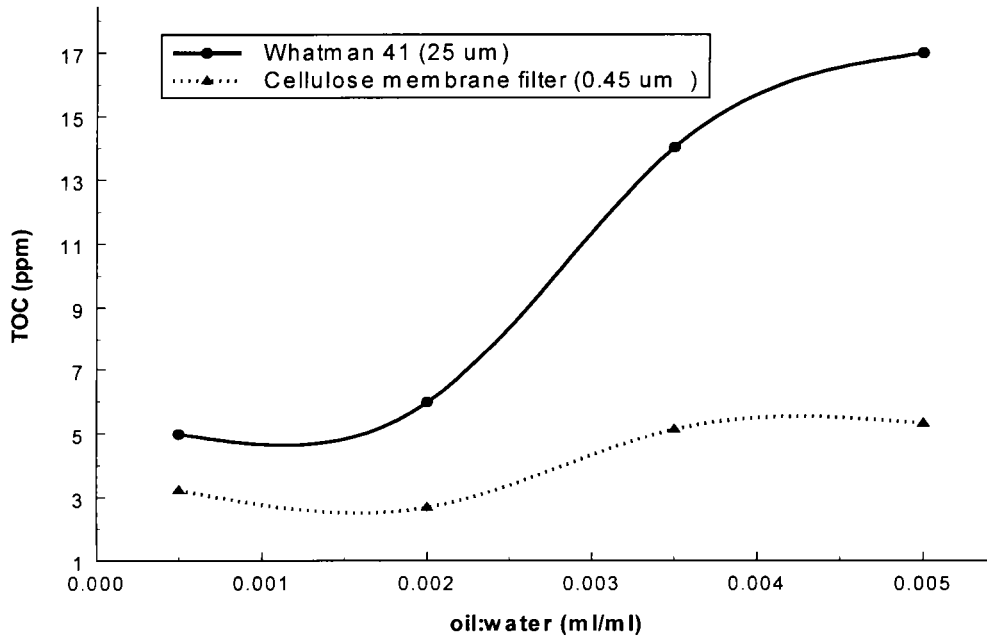


Figure 3: TOC concentration along the filtration curve of the laboratory extracted sample.

## EVALUATION OF ACTIVATED CARBON AND AMBERSORB 563

The laboratory tests have been performed in two 18 mm inside diameter U-shaped glass columns (to ensure constant flow rate and avoid beds drainage), with a constant level head reservoir and a Teflon valve. These columns allocate the activated carbon and have been previously cleaned with H<sub>2</sub>O<sub>2</sub> and distilled water.

**Table 3:** Typical properties for AMBERSORB 563 carbonaceous adsorbent

Physical form	black, spherical beads
Particle size distribution	20 to 50 mesh
Mean particle diameter (µm)	0.45
Bet surface area ( m <sup>2</sup> /g:)	550
Bulk density:(g/cc)	0.53
Crush Streng(g/bead).	>1000
Total pore volumen (cc/g)	0.60
Water adsorption( at 80% relative humidity).	10 %

**Table 4:** Typical properties for AMBERLITE IRA 67 weak base exchange resin

Matrix	crosslinked acrylic gel structure
Functional groups	Tertiary amines
Physical form	Transparent white beads.
Ionic form as shipped	Free base (FB).
Total exchange capacity	≥1,6 eq./L( FB form)
Moisture holding capacity	56 to 62 %( FB form)
Specific gravity	1.030 to 1.090 (FB form)
Bulk density	640 to 710g/L (FB form)

The feeding solutions have been prepared contacting water and oil in the proportions estimated from the plant reservoirs dimensions and experience. Given that, 3 cm<sup>3</sup> of oil and 1.8 L of water have been stirred during 30 min and the mixture, after sedimentation has been filtered through 25 µm filter paper (1.8 ppm of TOC).

With the purpose of setting up the differences between the products, rinsing experiments have been conducted at 10 BV/hr (Bed Volumes / hour) flow rate and are both plotted in Figure 4. In the Figure can be observed that both products have similar behaviour while releasing background TOC.

Also, the loading test of both products shows that even after 225 BV there is no TOC breakthrough above the background provided by the rinsing experiences on both substrates.

## EVALUATION OF IRA 67 ANIONIC RESIN

Rinsing and loading tests have been carried out on the IRA 67 for which the bed volume has had 2 cm<sup>3</sup> and the flow rates have been 10 BV/hr and 40 BV/hr respectively. Several feeding solutions have been prepared emulating the contaminants found in the station but in higher concentrations, as follows: (i) acetic acid solution (100 ppm), (ii) filtered water-extracted oil with 40 ppm of TOC and 80 ppm of acetic acid, (iii) filtered water-extracted oil with 20 ppm of TOC and 15 ppm of acetic acid.

The conductivity and concentration (by TOC and CG-MS) values have been followed in the effluent. Loading tests are plotted in Figure 5. The loading capacity of the resin for the acetic acid solution, curve (i), is 1 eq/L, lower than the one provided by the supplier, but that can be improved at lower charge rates. The curve shape is the expected for the simplest case analyzed.

Curve (ii), for a solution containing a very high oil concentration: 40 ppm of TOC (a value well over the one expected in a plant case) plus 80 ppm of acetic acid, shows from the start up, an effluent conductivity over curve (i).

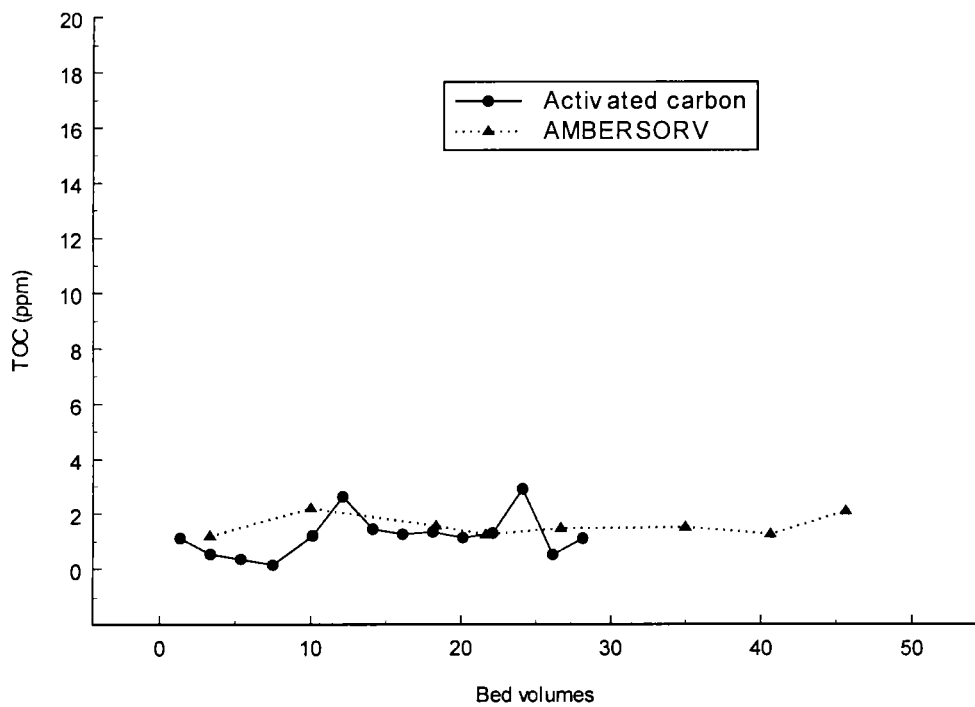


Figure 4: Rinsing tests of ACTIVATED CARBON and AMBERSORB 563

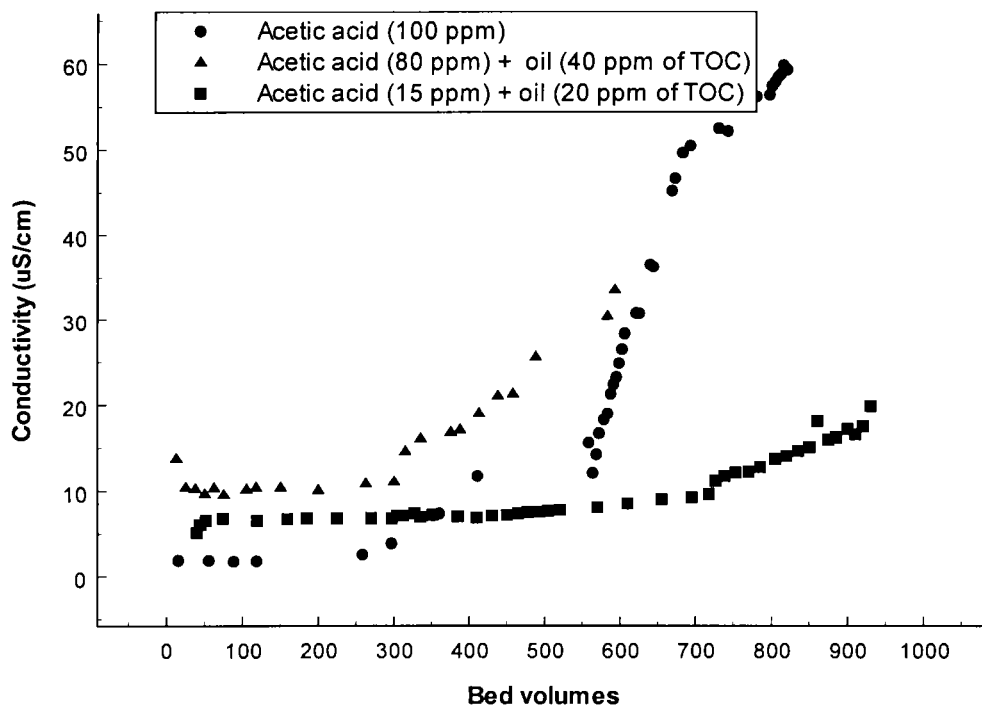


Figure 5: Loading tests of IRA 67 weak anionic resin

This have been explained through the behaviour of the oil polar compounds, that come from the additives, and are not properly retained by the weak resin. The values of acetic acid concentration obtained by CG-MS show that it is satisfactorily retained by the resin up to 300 BV. Then, the resin capacity lowers to approximately one half of the previous case.

The conditions of curve (iii), 15 ppm of acetic acid + 20 ppm of oil (TOC = 20 ppm), show the expected results according to the previous paragraph. That is, an intermediate conductivity since the start up and a delayed breakthrough.

## CONCLUSIONS

It has been the intention of the present paper to emphasize the widespread of requirements that can be fulfilled by a chemistry and processes support group to the NPPs corresponding sections. Through a recent example, it has been shown, how this local group should gather good knowledge of the facilities, equipments and draws while providing a relatively fast answer with local suppliers. That also manifests the need of good acquaintance to the country's technical market and its capability of providing the products in time.

Focusing in the heavy water upgrading system and the purification train, it has been found that: (i) The adsorbents studied here, have been both capable of reasonable performance showing no remarkable differences while tested under washing and oil retention conditions.

(ii) IRA 67 resin is a weak anionic resin that has proved to be capable of fixing acetic acid even under presence of organic matter originated in traces of oil. Polar compounds present in the water-oil extracted solution, in higher concentrations than the ones found in the plant, have not been fully retained by the resin. In the real case, the resin is located at the end of the purification train, that is at the polishing bed position, therefore showing proper operation for a given operating time.

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