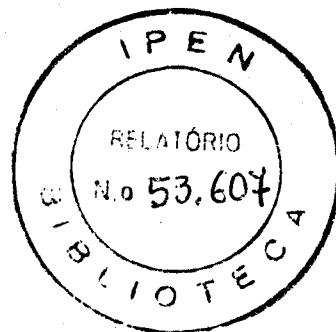


CHEMICAL SUPPORT AND MAINTENANCE WORK IN LIGHT-WATER MODERATED

RESEARCH REACTORS

Fausto Walter de Lima

Divisão de Radioquímica  
Instituto de Energia Atômica  
São Paulo - Brasil



Publicação IEA nº 119  
Dezembro - 1965

- 
- \* Presented at the Study Group Meeting on Research Reactor Operation and Maintenance Problems, promoted by the International Atomic Energy Agency and the Instituto Venezolano de Investigaciones Cientificas, Caracas, December 6-10, 1965.

Comissão Nacional de Energia Nuclear

Presidente: Prof.Dr. Luiz Cintra do Prado

Universidade de São Paulo

Reitor: Prof.Dr. Luiz Antonio da Gama e Silva

Instituto de Energia Atômica

Diretor: Prof.Dr. Rômulo Ribeiro Pieroni

Conselho Técnico-Científico do IEA

Prof.Dr. José Moura Gonçalves	}	pela USP
Prof.Dr. Walter Borzani		
Prof.Dr. Rui Ribeiro Franco	}	pela CNEN
Prof.Dr. Theodoreto H.I. de Arruda Souto		

Divisões Didático-Científicas

Divisão de Física Nuclear -

Chefe: Prof.Dr. Marcello D.S. Santos

Divisão de Radioquímica -

Chefe: Prof.Dr. Fausto Walter de Lima

Divisão de Radiobiologia -

Chefe: Prof.Dr. Rômulo Ribeiro Pieroni

Divisão de Metalurgia Nuclear -

Chefe: Prof.Dr. Tharcísio D.S. Santos

Divisão de Engenharia Química -

Chefe: Lic. Alcídio Abrão

Divisão de Engenharia Nuclear -

Chefe: Engº Pedro Bento de Camargo

Divisão de Operação e Manutenção de Reatores -

Chefe: Engº Azor Camargo Penteado Filho

Divisão de Ensino e Formação -

Chefe: Prof.Dr. Luiz Cintra do Prado (Licenciado)

CHEMICAL SUPPORT AND MAINTENANCE WORK IN LIGHT-WATER MODERATED

RESEARCH REACTORS \*

Fausto Walter de Lima

RESUMO

São revistos neste trabalho vários problemas ligados ao trabalho suporte e de manutenção para a operação de reatores de pesquisa. Examina-se o aspecto do Suporte Químico no caso particular do reator de pesquisa tipo piscina do Instituto de Energia Atômica, São Paulo. São examinados os problemas relacionados com o comportamento dos ladrilhos da piscina, purificação de água, análise de água, presença de produtos de fissão na água, corrosão de alumínio, química analítica, em relação a reatores tipo piscina.

RESUMÉ

Ce rapport resume les différents problèmes de maintenance liés au fonctionnement des réacteurs de recherche. Sont examinés, en particulier, les problèmes chimiques du réacteur type piscine de l'Institut de Energia Atômica, São Paulo.

Les auteurs traitent, en référence à quelques autres réacteurs, du comportement des carreaux, de la purification et analyse de l'eau, de la présence des produits de fission, de la corrosion de l'aluminium et de la chimie analytique.

---

\* Presented at the Study Group Meeting on Research Reactor Operation and Maintenance Problems, promoted by the International Atomic Energy Agency and the Instituto Venezolano de Investigaciones Científicas, Caracas, December 6-10, 1965.

## SUMMARY

Various problems in connection with support and maintenance work for the operation of research reactors are reviewed; in this review the aspect of Chemical Support is examined for the particular case of the IEA's (Atomic Energy Institute) swimming pool reactor.

Problems related to pool lining performance, water purification, water analysis, presence of fission products in the water, corrosion of aluminum, analytical chemistry, in connection with swimming pool reactors, are discussed.

### 1. INTRODUCTION

On the occasion of the IX General Conference of the International Atomic Energy Agency, held in September 1965, a group of participants had a get together in order to discuss some problems related to research reactors. Present were, among others, Dr. R. Hara, from the Japan Atomic Energy Research Institute, Dr. L. Yaffe, from the McGill University in Canada, both from the Agency, and myself. At that time somebody mentioned the troubles and difficulties people were having in putting into operation a research reactor in an Asian country. To this observation Dr. Yaffe reacted, almost immediately, with the following phrase (and I have his permission to quote him): "people have been building and using research reactors for a thousand years and they keep on doing the same mistakes! "How true ...

On that particular case and reactor it seems that hastiness orientated the operation of filling the pool with, supposedly, demineralized water. It so happened that the tap water to be demineralized was a little too heavy on the side of dissolved salts and alkalinity and after a few volumes had passed through the ion-exchanger resins, they required regeneration, which was not done.

The result was that the pool was filled, directly, with tap water of a not very good quality. pH was mentioned as being over 9.0! Corrosion started on beam tubes, which had to be changed, on aluminum frames, etc.

Troubles like that, and similar ones, unfortunately, still happen in all places where new research reactors are being built or put into operation.

Notices of algae growing in the water of swimming pool reactors, collapses of pool linings, improper handling of ion-exchangers, as in the case just mentioned, corrosion of fuel elements, etc. are always heard. Nevertheless, research reactors have to be put into operation and utilized and initial troubles and difficulties must, consequently, be faced and removed.

The theme of UTILIZATION of research reactors has been generously contemplated in various meetings, symposiums, etc., many of them promoted by the International Atomic Energy Agency.

However, one must bear in mind that before the UTILIZATION of research reactors is considered, OPERATION AND MAINTENANCE PROBLEMS have to be solved and adequately handled, if the reactor is ever to be utilized. Even after normal operation starts, service and maintenance problems are always present and if they are well managed and cared of a lot of headaches and unpleasant situations will be avoided.

On the line of support or services work for research reactors groups, Chemistry definitely does play a relevant and most important position. Obviously, a swimming pool reactor cannot operate without a water treatment staff or group. Various substances which are to be irradiated must be checked, prior to irradiation, for purity, neutron absorbers elements, thermal and chemical stability. Irradiation facilities, loops, must be examined for operating conditions, specially where situations in

which the deadly feared corrosion problems may take place. Fuel elements may fail, and they do, creating sometimes serious situations which can eventually be avoided if efficient control of fission products leakage is made. Many and various other examples could be listed in where Chemistry is of outmost importance for work around a research reactor.

The intention of this paper is to review and to report some work on the line of chemical service or support and maintenance problems based on the experience of the chemists group (Radiochemistry Division) of the "Instituto de Energia Atômica" (IEA), located in the city of São Paulo, Brazil. Such experience was accumulated during a period of about eight years of daily operation of the 5 Meggawatts swimming pool research reactor located in that Institute.

To adhere strictly to our own problems and/or our troubles we will discuss, in this paper, specially problems in connection with water treatment and water purification and the ones correlated to this topic, such as corrosion of aluminum pieces, control of fission products leakage and of fuel elements failure.

## 2. POOL LINING PERFORMANCE

Pool lining of the IEA's reactor is of the ceramic tile type, fixed with white cement. No special treatment was used to avoid contact of the tile joints with the pool water. It is known that in some reactors the tiles have been fixed in such a way that about a half centimeter was left in between tiles and this space is then filled with materials such as "Araldite". In the case of the IEA's reactor no such a step was ever taken and the tiles were rather well joined together with no special protection in between joints. Consequently, some contact in between water and cement takes place resulting in some leakage of cement; however, this leakage is very small and it is not sufficient to cause any

alteration of pH or resistivity of water.

Ceramic tile lining does not prevent, on an absolute way, penetration of water into the concrete walls of the pool and many reactors have faced serious problems of water leakage through the concrete walls. The best way to avoid this is to put an iron or mild steel sheet in the middle of the concrete shielding wall extending from the bottom of the pool up to the water level. This was done when of the construction of the reactor in the IEA, in 1956, and up to now the result has been excellent.

Adherence of tiles, up to this time, has been very good and no falling of tiles, after eight years of operation, was observed. However, it must be remembered that the pool has never been emptied during this time, except three months after the pool had been filled for the first time, eight years ago. Not emptying the pool may very well be the reason why no loosening of tiles has taken place since there have been cases, in other reactors, where whole tile sections of surface of various square meters have collapsed entirely by the time the pool had, for some reason, to be emptied. This falling of tile is supposed to be due to the hydrostatic pressure of the water imbibed into the concrete wall, hydrostatic pressure that is not counterbalanced by pressure on the other face of the lining since the pool is empty. It seems reasonable to suppose that this was the cause for this lining failure since it occurred in the bottom of the pool, by the time it was emptied, but not at the top. If the pool is not emptied, it seems that adherence of tiles is very good even when the water level has to be lowered for some feet, with consequent exposure of the corresponding tile surface; however, since in this case the hydrostatic pressure is very small and the lining is not pushed outwards.

Leaching of the tile itself does not seem to take place, at least to an extension that might be visually detected. Darkening

of the ceramic tile surface is observed if any strong radioactive source, such as spent fuel elements, is left near the wall. In this case some leaching of the tile surface seems to take place; the "image" of the tile is formed on the fuel element, probably due to the reaction of the silicate ions, which could have been leached from the tile and diffused into the water, with the aluminum of the fuel element cladding. However, this leaching must be very small, if any at all, since the total amount of silica found in the water, coming, supposedly, from leached tile, as well as from cement in the tile joints and external dust, is only about one part per million, what is perfectly reasonable for an opened pool reactor, (see Table III). Calcium and magnesium content in the water, and which might also come from dissolution of cement is also very low (See Table III).

References [1] and [2] should be consulted in connection with pool lining problems.

### 3. WATER CONDITION, TREATMENT AND MAINTENANCE AT THE IEA'S REACTOR

The water treatment system of the Brazilian swimming pool reactor is made up of two sets of purifying tanks. A primary system made up of the following components: a felt filter for gross filtration of suspended particles in the water, followed by a softener tank 1.5 m high by 0.75 m in diameter containing 400 liters of cationic ion-exchanger (sulphonic acid type); after the softener there is an activated carbon filter tank 1.5 m high by 0.50 m in diameter, followed by two ion-exchangers mixed-bed tanks, 1.5 m high by 0.50 m in diameter, each containing 60 liters of cationic and 60 liters of anionic ion-exchangers. One is kept in operation and the other on reserve to be used when the resin in the first is exhausted and needs regeneration.

The secondary system is made up of a tank of activated carbon filter 1.5 m high by 1.5 m in diameter followed by an ion-



exchanger mixed-bed tank 1.5 m high by 0.60 m in diameter containing 130 liters of cationic and 130 liters of anionic ion-exchanger. Another pair of tanks identical to this one is kept in reserve; when the resin in the first ion-exchanger tank is exhausted, water circulation is diverted to the second pair of tanks and the first is regenerated.

In the primary system tap water is first filtered from solid particles, softened, and then demineralized in the mixed-bed ion-exchanger at a rate of about 15 liters per minute. This treatment of the water in the primary system gives water with purity corresponding to one part per million of soluble substances. After passing through the primary system, the water is sent to the pool through stainless steel pipelines. Water from the pool is kept recirculating continuously through another set of mixed-bed ion-exchangers at a rate of about 60 liters per minute.

This water treatment system has been in operation for about eight years since the very beginning of the reactor's operation with no change of the original ion-exchanger resins set. No loss of efficiency has been observed in the primary or secondary system although this last one is submitted to radiation. Some loss of mass of the ion-exchangers took place but the amount lost is small and no replenishing with new exchanger has been made. This loss of mass is due to mechanical breakage of the resins granules during regeneration, in the primary and secondary system, and also, in the secondary, to some radiation damage, probably.

Regeneration is considered necessary when resistivity of the water in the outlet of the ion-exchanger tank is below  $5 \times 10^5$  ohm x cm. To maintain this pre-set condition, regeneration of the primary system, which purifies city tap water, is usually necessary when 30,000 liters of water has passed through the ion-exchanger. For the secondary system, whose function is repurifying the pool water continuously, working on a basis of 24 hours a

day, regeneration is required after a volume of about  $5 \times 10^6$  liters of water has passed through the tank. With these regeneration intervals pH of the water in the pool is maintained at  $6.2 \pm 0.1$ . When the cationic and anionic ion-exchangers are well mixed, the pH of the water at the outlet of the mixed-bed tank is about 7.0, a value in which corrosion of aluminum is not at its minimum. pH of the outlet water can be lowered down and conveniently controlled by letting some cationic exchanger to settle at the bottom of the tank without mixing it with the corresponding amount of anionic exchanger. This can be accomplished by slowly diminishing the air stream used to mix the resins after regeneration, instead of cutting out this stream suddenly when the two kinds of resins would be perfectly mixed. The well-known phenomenon of cationic leaking when the two kinds of resins are not perfectly mixed and some cationic resin is at the bottom of the tank, will provide the required amount of hydrogen ions to lower the pH.

Table I indicates a typical set of pH and resistivity determinations which are carried out daily.

Periodically the resins tanks are opened and small samples of the mixed ion-exchangers are taken for determination of capacity. No appreciable loss of capacity has been observed for the strong acid (cationic) and strong base (anionic) type of exchangers, whose capacities are about 4.8 meq/g and 3.0 meq/g, respectively.

Checking of performance of the secondary ion-exchanger resin is also made by a weekly determination of decontamination capacity, measuring the gamma and beta activity of the inlet water (pool water) and of the outlet water and determining the decontamination factor by taking the quotient of those two values for the same volume of water. The same decontamination factor is also determined in laboratory ion-exchangers columns, with new resins of the same kind as the ones used in the secondary system

and placed in small columns with height, diameter and flow rate in proportion to the actual treatment system. Laboratory determination of decontamination factor is carried out at the same temperature of the pool water, i.e., 32-35°C. The gamma decontamination factors varies from  $2 \times 10^3$ , for a resin near to regeneration time, to  $7 \times 10^3$  for a recently regenerated resin. Beta decontamination factors are even larger than the gamma factors. Values of laboratory decontamination factors and the ones in the secondary water treatment system are practically the same indicating still good working conditions of the purification system.

TABLE I

DAILY pH AND RESISTIVITY DETERMINATION

DATE	pH			RESISTIVITY (ohm x cm) $10^{-5}$		
	PRIMARY	POOL	SECONDARY	PRIMARY	POOL	SECONDARY
1-10	5.6	6.2	5.8	11.3	7.9	>16.0
4-10	5.6	6.1	5.7	10.0	9.4	>16.0
5-10	5.5	6.2	5.8	12.8	10.6	>16.0
6-10	5.4	6.2	5.7	5.7	10.6	>16.0
7-10	5.4	6.2	5.7	9.0	8.8	10.8
8-10	5.4	6.2	5.8	8.7	8.1	>16.0
11-10	5.6	6.2	5.8	11.1	8.6	>16.0
12-10	5.5	6.2	5.7	5.6	9.7	>16.0
13-10	5.0	6.2	5.7	3.2	9.2	>16.0 <sup>Ⓞ</sup>
14-10	5.0	6.0	5.7	4.0	7.2	>16.0
15-10	5.1	6.0	5.7	4.0	8.7	>16.0
18-10	5.4	6.1	5.8	5.6	9.7	>16.0
19-10	5.4	6.2	5.8	7.2	10.5	>16.0
20-10	5.4	6.2	5.8	8.0	9.6	>16.0
21-10	5.4	6.1	5.7	9.4	6.4	>16.0
22-10	5.4	6.1	5.7	9.7	6.4	>16.0
25-10	5.4	6.2	5.8	8.0	8.7	>16.0
27-10	5.4	6.2	5.7	9.4	9.5	>16.0
28-10	5.4	6.2	5.8	9.4	8.1	>16.0
29-10	5.4	6.2	5.8	9.7	7.2	>16.0

Table II is a typical set of values for determination of gamma decontamination factors.

TABLE II

DETERMINATION OF GAMMA DECONTAMINATION FACTORS

DATE	VOLUME OF WATER TREATED (LITERS)	COUNTS/LITER MIN.			DECONTAMINATION FACTOR		POWER (mw)	OPERATING TIME (h)	t <sub>000</sub> (h)
		P <sub>00</sub>	C <sub>00</sub>	S <sub>00</sub>	P/C	P/S			
1-10	SB <sub>0</sub> 3.5 x 10 <sup>6</sup>	284,230	279,300	37	1.0	7.7 x 10 <sup>3</sup>	2	16	14
8-10	SA <sub>0</sub> 3.0 x 10 <sup>5</sup>	279,790	274,440	165	1.0	1.7 x 10 <sup>3</sup>	2	16	14
15-10	SA 1.0 x 10 <sup>6</sup>	283,090	279,615	52	1.0	5.5 x 10 <sup>3</sup>	2	16	14
22-10	SA 1.7 x 10 <sup>6</sup>	292,550	273,676	98	1.1	3.2 x 10 <sup>3</sup>	2	16	14
29-10	SA 2.2 x 10 <sup>6</sup>	376,950	334,235	267	1.1	1.4 x 10 <sup>3</sup>	2	16	14

SB<sub>0</sub> and SA<sub>0</sub> = Secondary B unity and Secondary A unity, respectively.

P<sub>00</sub> = Pool water.

C<sub>00</sub> = Pool water after passing in the carbon filter.

S<sub>00</sub> = Secondary water.

t<sub>000</sub> = Time of sampling after reactor shut down.

Location of the water treatment system in the basement of the reactor building does not seem to be the best solution, since the basement is not accessible during the operation of the reactor. A water treatment house outside the reactor building would allow access to the place while the reactor is in operation, although only for situations of emergency, since the repurification piping circuit is radioactive.

#### 4. WATER CHEMICAL ANALYSIS

Besides the daily determination of pH and resistivity, the pool water is analysed for some important elements such as copper, iron and chlorine owing to their pernicious effect on aluminum as far as corrosion of this last element is concerned. 2 parts per million of copper ion or 0.1 part per million of chlorine ion is sufficient to start pit corrosion on aluminum. Mercury would also be a very dangerous element to the integrity of aluminum; however, no routine analysis for this element is carried out since no irradiation of mercury has been made. In case the necessity of mercury irradiation arises special care must be exercised for this particular irradiation.

Aluminum is also routinely analysed in the water since an increase of its concentration would indicate serious corrosion in some part (aluminum frames, beam tubes, storage racks, etc.).

Silica and organic matter are also determined weekly. Increase in silica may indicate leaching of tiles or exposure of cement to the water. Presence of organic matter would create favourable conditions for microorganism growth (algae) and might also give turbidity to the water making difficult normal operations of equipment that have to be handled inside the pool.

Parts per million of total soluble substance (ionisable) in water can be calculated by means of resistivity measurements.

Solid residue is determined at three temperatures, 100, 500 and 300° C.

Analytical methods used for the various elements or substances are activation methods for chlorine and copper and colorimetric for aluminum, iron and silica. Organic matter is determined volumetrically by permanganometry.

All these analyses are carried out not only for the pool water but also for the primary and secondary water. A large difference in analysis values found, for instance, for primary or secondary water, as compared to the pool water, would indicate abnormal conditions which should be cared for and corrected.

Cleaning of the bottom of the pool is carried out once a month by a "vacuum cleaner" type of apparatus which removes fine particles deposited in the bottom.

Table III is a typical set of values for the analyses mentioned. These tables are routinely filled in each month.

## 5. DETECTION OF FISSION PRODUCTS IN THE WATER

Fuel elements failure is always possible. A permanent check of the presence and concentration of fission products in the water, of swimming pool reactors may indicate defective fuel elements before liberation of those fission products into the water, and in the air reaches a value that would indicate the need to take serious steps, such as evacuation of buildings.

Commercial types of equipment, although rather expensive, are very efficient for the finality of a continuous checking of liberation of fission products in the water. However, "home made" systems can be of high value and can be built with very little expenditure.

TABLE III  
MONTHLY WATER ANALYSIS

	DATE	TAP WATER ( ppm )	PRIMARY (ppm)	POOL ( ppm )	SECONDARY ( ppm )
COPPER	28-10	0.02	0.0004	0.0002	0.0009
CHLORINE	28-10	0.13	0.0033	0.0009	0.0006
ALUMINUM	7-10	0.500	0.005	0.025	0.010
	15-10		0.010	0.010	0.005
	22-10		0.005	0.010	0.005
	27-10		0.015	0.020	0.010
IRON	25-10	0.090	0.050	0.010	0.005
ORGANIC MATTER	6-10	2.50	1.00	2.30	0.80
	13-10	2.50	1.80	1.70	0.60
	20-10	1.50	0.80	1.50	0.60
	26-10	1.90	0.80	1.80	0.50
SILICA	5-10	4.00	0.60	2.40	2.45
	19-10		0.30	0.60	0.15
	27-10		3.55	1.20	0.60
TOTAL SOLIDS	25-10	100°C 41.1		100°C 2.3	100°C 1.8
		500°C 28.4		500°C 1.7	500°C 1.2
		800°C 18.0		800°C 1.6	800°C 1.0
	28-10		100°C 5.1		
			500°C 4.2		
			800°C 3.7		
HARDNESS	28-10	6.30	<0.1	<0.1	<0.1

The system used at the IEA's reactor consists of a by pass in the water refrigerating circuit in which water, that had passed directly through the reactor nucleus, is directed to small plastic columns containing appropriate retention material for some specific fission product. Anionic ion-exchangers are frequently used but they have the inconvenience of retaining too many anions whose radiations will mask the ones emitted by the specific fission product which is being sought for. Fission iodine radio-

isotopes are usually used as the indicating isotopes for liberation of fission products in the water and although, as said, they could be collected in anion-exchangers, silver chloride columns are used instead, in the IEA's detection system. The silver chloride columns are prepared by passing a silver nitrate solution through a cationic ion-exchanger resin. The silver saturated resin is next treated by hydrochloric acid and then the resin grains are calcined at 300° C. The granules of silver left have appropriate granulometry if a cationic ion-exchanger of 50 to 100 meshes is used.

In fact the silver chloride columns thus prepared retain also, besides the radioiodine isotopes, the ions chlorine, bromine, niobium, manganese, chromium, magnesium and zirconium. However, a washing of the column with a mixture of nitric acid 0.1 molar and hydrofluoric acid 0.1 molar removes manganese, magnesium, chromium, zirconium and niobium. Chlorine and bromine radioisotopes remains in the column together with the fission radioiodines. The amount of chlorine in the water is very small (see Table III) and it does not interfere with the test. Bromine fission products have nuclear characteristics such as fission yield, half-life and gamma energy peaks that do not interfere with the detection of iodine isotopes.

Silver chloride columns thus prepared and after being used in the fission products detection system, are removed from the circuit and taken to the laboratory for measurement, during the operation of the reactor. New columns are put in the circuit and as many checks as desired can be run during the reactor's operation. Gamma spectrometry determination is carried out looking for the peaks of radioiodine fission isotopes, I-131, I-132, I-133, I-135.

Indications of fuel elements failure have not been observed and of the fission iodine radioisotopes, only Iodine-131 has been detected by the system just described. Iodine-131 comes, probably, from some escape or contamination during the irradiation of telluric acid for the production of Iodine-131. However, the quantity of this last isotope in the water is very small, amounting



to  $2 \times 10^{-4}$  micromicro curies per milliliter, which is smaller than the activity of iodine found in many other reactors.

The system described, although not giving a continuous indication, is simple and inexpensive enough to be installed in any swimming pool research reactor. Check of the detection sensitivity of this system was made by adding 3 millicuries of iodine in the pool (270,000 liters) with the reactor shut down. After homogenization of the pool water the detection system was made to work and it indicated an increase in activity of Iodine-131 for the amount corresponding to the one added, with an accuracy better than 10%.

Water treatment, detection of fission products and water analysis problems are also examined in reference [3], [4], [5], [6], [7], [8].

## 6. CORROSION PROBLEMS

Problems of corrosion, specially aluminum corrosion, occurred in swimming pool reactors. In general those problems were caused by situations which were far removed from the ones that are considered normal in the operation and maintenance of reactors, such as using exhausted ion-exchangers resins, immersing into the water pieces of equipment or fuel elements from which soldering flux was not adequately removed, contact in between aluminum and more noble metals, accidents in irradiation of mercury, too high temperature maintained in aluminum irradiation facilities, use of pieces of aluminum under stress etc. If working and operating conditions are adequate aluminum will not corrode in any extensive amount in deionised water, whatever may be the use given to it, whether in beam tubes, equipment or cladding of fuel elements.

Some serious problems of corrosion provoked by poor removal of soldering flux in the first set of the IEA's reactor

fuel elements were faced and they have been described elsewhere [8]. We had also some problems of minor consequences concerning the corrosion of aluminum tubes used for containment of spent fuel elements. This corrosion was caused by contact of lead, used as ballast inside the tubes, and which were accidentally filled with water, and the aluminum tubes. No serious consequences resulted, except liberation of precipitate of aluminum hydroxide into the pool when the pool water and the water inside the tubes came to be in contact. The containment aluminum tubes were later removed from the pool with no bad results for the other aluminum equipment or fuel elements immersed in the pool.

A darkening on the surface of some aluminum pieces existing in the water has appeared. Trying to repeat, in experimental conditions, this phenomenon, using aluminum sheets or coupons of about 3 x 3 x 0.2 centimeters, it has been observed that, in general, the sheets which were cold rolled and which did not suffer any subsequent thermal treatment were the ones that would preferentially get darkened.

Since the phenomenon was definitely more pronounced in the sheets which had suffered cold rolling treatment it was thought that the darkening could have been caused by stress corrosion, since the cold rolling operation, not followed by any thermal treatment, would leave the aluminum surface under a state of strain. ©

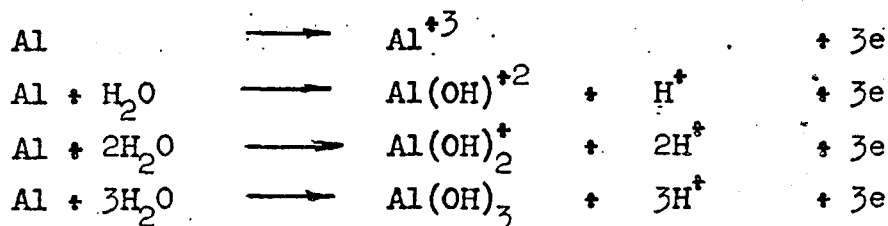
A uniform piece of metal may be so only apparently, and any portion of the metal which has been subjected to strain is less noble than an unstrained portion. Crystals of different sizes may be present in the metal, the small crystals being less noble than the larger ones. Inclusions of minute amounts of more noble metals may also occur in relatively pure metals. These inclusions may be introduced during metallurgical operations if these operations are carried out in machinery or equipment which are not absolutely clean and free from other metals contamination.

The existence of these more noble portions will set up local voltaic cells, with cathodic and anodic regions in the metal surface, and if a depolarizer is present, in the water where the metal is immersed, corrosion of the anodic region will occur.

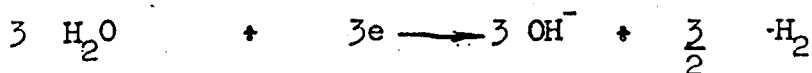
Presence of anodic and cathodic parts in the pieces which had darkened could not be shown directly since they belonged to aluminum pieces which could not be removed from the pool or to equipment from which samples could not be taken without sacrificing the entire piece or equipment. However, the presence of anodic and cathodic parts in the aluminum sheets or coupons mentioned before, which had been cold rolled and subjected to strain or the ones having iron inclusions on the surface, could be demonstrated by means of "color indicators" (phenolphthalein or alizarine) dispersed in agar. The "indicator" is prepared by dissolving 20 to 30 grams of bacteriologically pure agar in one liter of hot water and to which 5 grams of sodium chloride and 2 milliliter of a 5% alcoholic solution of phenolphthalein are added. The warm solution is poured over the aluminum coupon and left to cool off when the agar will form a jelly.

If there are anodic and cathodic parts in the aluminum coupons, aluminum will dissolve in the anodic region while at the cathodic the concentration of hydroxyl ions will increase in accordance to the following reactions:

Anodic region



Cathodic region



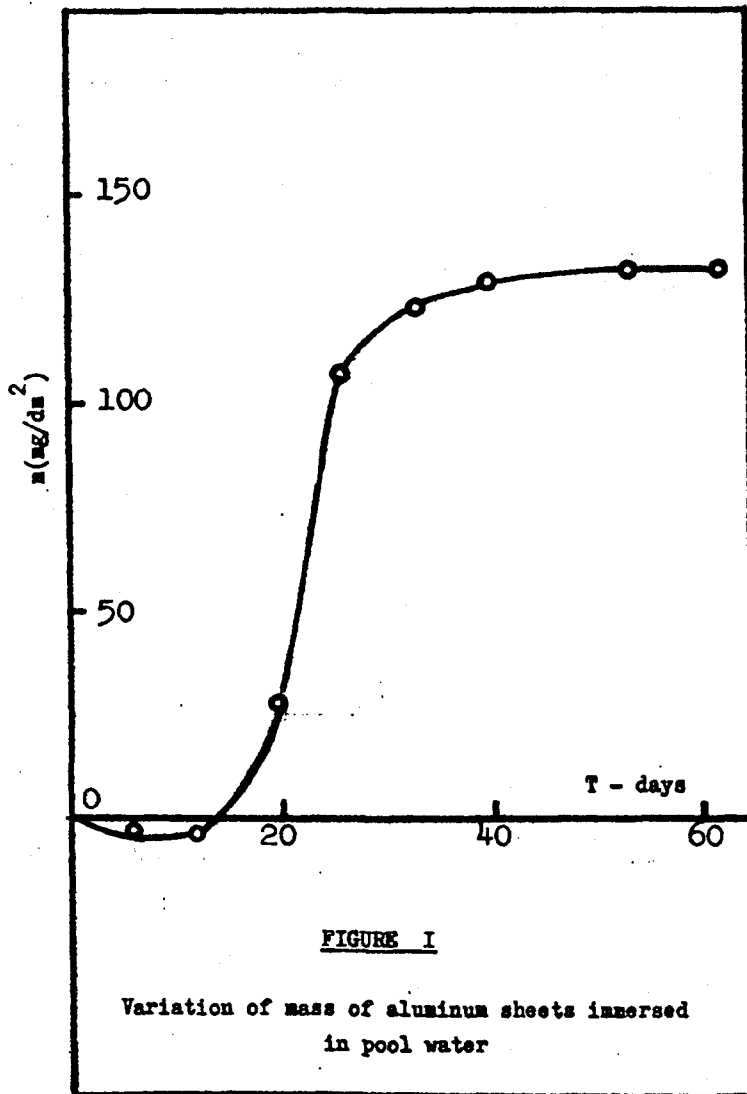
Owing to the presence of the phenolphthalein the hydroxyl ions at the cathodic region will give a pink color to that region. The sodium chloride present in the agar serves as a conductor and the agar jelly will prevent the diffusion of the formed ions, allowing the formation of color only in the cathodic region.

In order to create a definitely state of strain in the aluminum coupons, a depression of one centimeter diameter and one millimeter deep was made at one end of some of the aluminum coupons. The other ones were just left with the strain caused by the cold rolling. In all of them the color indicator test was positive, the cathodic region being the place where the mechanical depression was made. If the strain was removed, prior to the test, by annealing the aluminum coupons, the test was always negative.

The indicator test was also positive if the aluminum coupons had been prepared taking the samples from aluminum sheets which had other metallic inclusions, introduced during the metallurgical work. It was also positive if the sheets had suffered any handling that would introduce surface roughening.

To observe the behaviour of the darkened aluminum coupons on a long time basis, various coupons samples (Alloy 1100 or 2 S) have been put in the pool water hanging by means of nylon fishing lines for various lengths of time. It is observed that the coupons with strain introduced by cold rolling will get darkened after about 72 hours they have been immersed in the pool. The darkening would then slowly disappear leaving the coupons with the original aspect but with a dull surface and not the bright original one. Samples have been kept within the water up to 3,000 hours. They are removed from the water every week and checked for variation in weight; there is a small decreasing in weight on the first fifteen days and the weight rises again and remains constant after about twenty or thirty days. (Figure I) No visual pitting or general corrosion is observed on the specimen. Photomicrograph does not show

any attack to the aluminum piece itself showing that the darkening is only of superficial effect, which is in accordance to the long range test in which no corrosion of the aluminum was observed (exposure test of 3,000 hours). Similar tests have been made by Neuman [9] for aluminum alloy 1100 as well as for 3003, 5052, 5154, 6061.



Although the darkening of the aluminum may cause apprehension when first observed, it is, by itself, of minor or secondary importance.

Many unpleasant experiences have occurred in various swimming pool reactors, all over the world, concerning corrosion, but the phenomenon is perfectly avoidable. With suitable water treatment and cleanliness of the pool, as well as of the equipment or pieces of aluminum or other material introduced in the water, no reason for fear of corrosion should prevail.

One must bear in mind, however, that only water purity and cleanliness of the pool will not be a guarantee against corrosion if the equipment or piece of aluminum or other metal have been badly handled. Pieces under strain, microscopic metallic inclusions coming from rolling mills not adequately clean, inhomogeneities or mechanical defects, surface roughening, surface contamination and other fabrication factors may be causes for corrosion troubles which will be difficult to trace. Misleading situations may have to be faced since the first thing one looks into, when a corrosion problem appears, is the water condition, with no due regard to the other causes just mentioned; if the water condition is normal, fabrication causes for corrosion (metallic inclusions, strain, surface roughening) should be looked for.

One should not consider a luxury any extra care taken to deal with material that have to be put into the water. Aluminum pieces should always be handled with gloves, preferable white ones; as soon as they are not whitish anymore they should be changed for new ones. Handling of aluminum with bare hands will cause contamination of the piece with sodium chloride, usually together with some natural grease from the hands. If the aluminum piece to be put into the water is a fuel element the remarks just made should be doubly enforced by those responsible for the various operations.

Static or stagnant water, even if its condition is very

good, should not be left in contact with aluminum. Contamination on the aluminum surface will dissolve and will not diffuse rapidly enough to avoid formation of zones of different concentrations, around the aluminum, setting up concentration cells. Agitation of the water around the aluminum piece will prevent existence of zones of differential concentration.

If any bad handling of aluminum has caused the protective layer of aluminum oxide to be removed, for instance, by wrongly using aggressive cleaning agents or steel brushes, a treatment with some oxidation product such as magnesium or sodium chromate or nitric acid solution must be done to restore the oxide layer. References [9], [10], [11] and [12] should be consulted in connection to the handling of aluminum pieces and equipment, as well as aluminum-clad fuel elements, in order to avoid conditions which are propitious for corrosion when aluminum is immersed in demineralized water.

## 7. ANALYTICAL CHEMISTRY SUPPORT WORK TO RESEARCH REACTORS

Several analytical chemistry problems arise in connection with operation of research reactors and research programs being developed in reactor's engineering, physics, metallurgy, etc. Approach to the solution for those problems may be made by classical Analytical Chemistry or by Radiochemical Methods. However, advantage should be taken, by Chemists in charge of this analytical support work, of the proximity of the reactor. Radiochemical analytical methods should be developed and applied to solve those problems mentioned and that arise in connection with the operation of the reactor or with the development of research programs of other groups.

A large percentage of the analytical problems of groups working around a research reactor, is connected with the determination of very small amounts of substances. Exemples have already

been given of the determination of some elements, in the water of swimming pool reactors, at concentrations of parts per million or even parts per billion.

For those kind of problems activation analysis is extremely important. Sensitivity of activation methods are seldom superseded by other methods. Application of activation methods in places not provided with adequate facilities, such as counting equipment, not to say of the proximity of a reactor, might not be the best solution. However, for a chemical and radiochemical group working in an institution provided with the reactor and, consequently, with access to counting equipment, radiochemical methods should deserve some preference over other more classical methods. Laboratory facilities in new research reactors centers may not be very abundant, specially in developing countries, but counting equipment must always be present in reactor's centers since the very beginning life of the laboratories.

In fact radiochemical analytical methods are in a position that today they may even be considered classical, also. No labelling of sophistication should be applied to those methods. Many symposiums and international conferences have already demonstrated "ad abundantia" the solid and firm position of radiochemical analytical methods, particularly of activation analysis. ©

Chlorine, copper and silver, for instance, and which are important elements whose presence should always be checked in the water of swimming pool reactors, may be easily and routinely analysed by activation methods. In the case of the IEA's reactor copper and chlorine are analysed weekly by activation methods, taking no more than one-man-hour for the analysis of both elements [13].

Application of radiochemical methods, in reactor's centers, may also serve the dual purpose of the analysis in itself and for the no less important aim of training of radiochemists,



creating in new personnel attached to such centers a philosophy of radiochemical approach to chemical problems. I might be a little biased but I think a group of chemists working in a research reactor center should think and react instinctively for a radiochemical solution and approach to analytical problems that may come to their hands, as requests of other groups developing their activities around the reactor.

.....

The purpose of this paper was not of covering the complete spectrum of maintenance and support chemical work around a research reactor, but rather of focalizing attention on some actual situations or problems that the chemical group at the Atomic Energy Institute had to face.

As already mentioned by Hara [5] activities of chemists in a research reactor group involve two broad aspects: first, research in itself; and second, work necessary for the operation and maintenance of the reactor, extending these last activities also to the preparation necessary for the performance of specialized research.

In large institutions it is not unlikely that pure research chemists are not going to get mingled with, apparently, not so noble functions as support work. However, shortage of people is an always present problem and, sometimes, an acute one, specially in new research reactors centers. It is not uncommon that people, in those centers, have to share or distribute their time in such a way to attend research problems and support work to the institution or to other groups. I believe that many scientists, engineers and others in various South American countries do understand me. ©

A decade or so, many of us, in our own countries, got

together and, full of enthusiasm, started, literally from bare ground, to build up atomic energy institutions. Most of us were coming from university duties. It was not thought that much difference in our way of working would be found in the novel institutions and that our own research lines would continue or be resumed after the stage of steady state operation of the reactor had been reached. Well, in many cases it did not work out exactly that way, and we had to sacrifice part of our own scientific ambitions so the group would develop harmoniously, as a whole. Radioisotopes for medical uses had to be produced, water had to be treated, emergency situations had to be faced, training of new people had to be done, consultation problems put up by industries had to be solved. For a good number of years general support work to the reactor's group or to other groups such as biologists, physicists, metallurgists, etc., occupied a large percentage of time of the radiochemists at the Atomic Energy Institute, in São Paulo.

The work in itself is not of a routine nature and uninteresting. Quite on the contrary: being unexpected situations they do require quite a lot of ingenuity for the approach and solution of the problem. Practically all proposed problems or situations that arose by the use and operation of the reactor turned out to be an excellent theme for applied research on one subject or another. For instance, prevention of corrosion of aluminum forced to search for elements in very low concentration; methods of analysis had to be developed for that particular situation; training of new people and students was carried out using those actual problems as small research projects that, very often, turned out to be worth of publication in high standards scientific journals. Great was the number of situations like that.

Going back to some lines behind and using the same words, and ideas linked to words such as "noble work and noble functions" I am definitely sure that operation and maintenance aspects of activities around a research reactor are not a "plebeian" activity.

The most definite proof of that is this gathering of people interested in Operation and Maintenance Problems of Research Reactor and formed by, with the exception of the speaker, the best qualified scientists from all over the world.

#### 8. BIBLIOGRAPHICAL REFERENCES

- [1] CARON, P. et PLATZER, R., Épuration d'Eau et Revêtements, Bull. Inf. Sci. Tech. 32, 53. (1959).
- [2] BREASEALE, W.M., Some Considerations Involved in the Design of Swimming Pool Research Reactors, Babcock and Wilcox, (1960).
- [3] PROKSCH, E. and BILDSTEIN, H., General Areas Needing Chemical Competence to Support Reactor Operation, Chemistry Research and Chemical Techniques Based on Research Reactors, Technical Report Series N. 17, IAEA Publication, 1963.
- [4] PROKSCH, E., Purification of Reactor Moderator-Coolants, Atomic Energy Review 1, N. 1, 5 (1963).
- [5] HARA, R., Chemistry Research Based on Research Reactors, Atomic Energy Review 1, N.1, 93 (1963). ©
- [6] AYBERS, N.M., Radioactivity Problems Associated With Installation, Operation and Maintenance of Research Reactors, Symposium on Programming and Utilization of Research Reactors, Vienna, October, 1961.
- [7] LIMA, F.W., Development of Radiochemistry Activities in New Research Reactors Centers, presented at the Study Group Meeting on the Utilization of Research, São Paulo, Brazil, November 1963, IEA Pub. n. 100.

- [8] LIMA, F.W., Chemical Problems Arising in the Use of a Swimming Pool Research Reactor and Uses of the Reactor in Chemistry, Symposium on Programming and Utilization of Research Reactors, Vienna, October 1961.
- [9] NEUMAN, P.D., The Corrosion of Aluminum Alloys in the Oak Ridge Research Reactor, ORNL 3151, June 23, 1961.
- [10] BERGSTRESSER, M.E., Aluminum Corrosion in Subcritical and Zero Power Critical Reactors, TID-4500, 31st ed., July 1964.
- [11] CORIOU, H., Les Problèmes de Corrosion dans les Piles Piscines, Bull. Inf. Sci. Tech. 35, 47 (1959).
- [12] LÉON, J.M.F., y SAVIRÓN, E.A., Detección de Radioelementos en el Agua del Reactor de Piscina JEN-1, Proceedings of a Study Group Meeting on Utilization of Research Reactors, São Paulo, Brazil, November 1963. IAEA Publication, Vienna, 1965.
- [13] GIAMBASTIANI, R., SILVA Fº, J.G. da, and LIMA, F.W., Determination of Chlorine and Copper in High Purity Water by Radioactivation Analysis, IEA Pub. nº 97.