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“Danube WATER Integrated Management”

TECHNICAL REPORT no. 3

Sub activity 12.3 Testing the technology for wastewater processing and the technology for conditioning the liquid organic wastes from the nuclear plants Cernavoda and Kozloduy, using the installation for wastes processing from RATEN-ICN.

Leader of working group for Activity 12: National Research & Development Institute for Chemistry & Petrochemistry – ICECHIM – PP6

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1. INTRODUCTION.

In Romania is in force the Order no. 156/2005 of CNCAN President for approval of regulation on the classification of radioactive waste.

Our activity refers to low level waste, which contains radioactive and non-radioactive components that may affect humans and the environment. Therefore the management of such wastes should take into account both radioactive and non-radioactive components and their associated hazards.

At **Cernavoda NPP** [1] radioactive wastes waters **level 1** - from the laundry, underground drainage pits of the spent fuel bay, the underground drainage pits of shower rooms, laboratories, floor drainage, with radioactivity ranging between **3.7×10^2 Bq/l and 3.7×10^{-1} Bq/l** and **level 2** from the heavy water upgrading system, the equipment decontamination system, rubber objects laundry with radioactivity ranging between 3.7×10^4 Bq/l and 3.7×10 Bq/l.. **Level 3** are higher radioactive wastes - resulting from the reactor drainage systems, spent fuel storage bays, spent resin storage vaults, whose radioactivity ranging between 3.7×10^6 Bq/l and 3.7×10^4 Bq/l.

Kozloduy NPP [2] have WWER-440 and WWER-1000 reactor units. These were constructed using a “double-unit” concept — two reactors, one common auxiliary building.

The ion exchange **resin** is used in the water purification system both in nuclear research and power reactors. Combined with active carbon, the resin removes the dissolved elements from water when the nuclear reactor is operating. After its consumption, it becomes a special type of radioactive waste. The usual treatment of this type of waste is the immobilization with Portland cement, which is simple and low cost. However, its low capacity of immobilization and the increase volume of waste have been the challenges.

For the conditioning of ion-exchangers generated from operation of Cernavoda NPP Unit 1 techniques of direct immobilization in cement, bitumen and organic polymers have been experimented within ICN Pitesti. The selected process for conditioning of

spent resins is their bituminization. In view of final disposal, the container that includes the waste bitumen block is cemented and confined in another with a larger capacity [3].

According to those above presented, we focused in this project on developing an efficient technology, based on ion exchange resin (nuclear use type), for **decontamination of radwaste waters resulting from Cernavoda and Kozloduy NPP.**

The experimental works performed at sub activity 12.3 concerning the testing of the technology for decontaminating radioactive aqueous waste had two objectives:

- Establishing influence the pH of the aqueous waste, containing cobalt on exchange capacity of the ion exchange resins. The determinations were performed in simulated non-radioactive system at ICECHIM- PP6 laboratories;
- Testing technology for decontamination radioactive waste water, obtained from the Cernavoda plant, respectively Kozloduy in the pilot installations from ICN-PP7, INRNE Bg - PP13.

In parallel, UPB-PP8 developed the theoretical basis of the equipment necessary for application of the technology. Also, UPB-PP8 performed modeling of tritium extraction.

The partners established the technology for decontamination of low level aqueous radioactive wastes.

In the field of **organic liquid radwastes** the works were focused on mineral waste oils, coming from Cernavoda NPP which contain variables amounts of water (practical water in oil type emulsion) mixed with tritium (as tritiated water).

In the previous works were established a new technology based on two phases:

- the removal of water and tritiated water from spent oil by breaking the emulsion followed by oil dehydration. The experimental technique was based on testing and selection of a demulsifiers. Demulsifiers selection and establishing optimum process parameters were made first in non-radioactive conditions (at ICECHIM) and then on radioactive waste at RATEN-ICN, where was determinate the reducing of the tritium content of the oil wastes.
- Sorption of decontaminated oil, resulting from the first phase upon polimer ; selection of polymer (RATEN-ICN contributions). Waste oil with a concentration of tritium activity above the clearance limit can be immobilized in a suitable absorbent

polymer for transportation across border at external operators for incineration. This work is aimed at demonstrating the feasibility of decontamination of waste oils by means of washing with different decontamination agents and drying in vacuum. The treatment technology of waste oils from Cernavoda NPP is applicable when the value of tritium concentration is higher than clearance limit or is above level of acceptance to treatment by incineration.

The works performed at sub activity 12.3 in the field of conditioning of the spent oil consist in testing the second phase of the technology – sorption of the decontaminated oil. These works were carried at ICN-PP7.

In Nuclear Power Station large volumes of waste oils are accumulating during normal operation and during maintenance operations. In the CANDU Nuclear Power Station, some of this waste oils are found to be contaminated with tritium. The waste oil with a concentration of tritium activity above the clearance limit can be immobilized in a suitable absorbent polymer for transportation in view of treatment by incineration. The treatment technology of waste oils from Cernavoda NPP is applicable when the value of tritium concentration is higher than clearance limit or is above level of acceptance to treatment by incineration.

This report provides an analysis of performance of the Waste Lock® 770/OrganoLock™ absorbent polymer technology. The technology was demonstrated at the Institute for Nuclear Research subsidiary of the Autonomous Company of Technologies for Nuclear Energy – Institute for Nuclear Research (RATEN ICN) Romania to determine whether it can be used as an absorbent and solidification agent for the organic liquid waste, to provide a substitute or equivalent for current Nochar PetroBond® technology at Cernavoda NPP.

This technical report summarizes the works for assessment the technology for solidify the organic liquid waste contaminated with tritium using absorbent polymers according with subactivity 12.3 - “Testing the technology for conditioning the liquid organic waste from the nuclear plants Cernavoda and Kozloduy, using the installation for the waste processing from RATEN-ICN” objective of the Activity 12 "Elaboration of a new technology for wastewater processing and conditioning the organic liquid wastes

radioactively contaminated from nuclear power plants", within cross-border Romania Bulgaria MIS-ETC WATER 161 project - Danube Water Integrated Management.

2. Experimental works performed at ICECHIM

Experiments in simulated non radioactive system were conducted in an installation consisting of:

- glass column containing ion exchange resin with inner diameter of 1.8 cm and height of 20 cm. The resin volume was by 12,72 cm³ and the flow passage of the solution through the ion exchange resin was varied between 1,03 and 2,18 cm³/min
- dropping funnel with a volume of 500 mL, for transfer the solution (simulated) containing cobalt ions into the glass column;
- collection vessel for effluent.

In the experiments were tested the ion exchange resins Purolite NRW 1600 from Purolite Comp:

The experiments were presented in table 1 and in the fig 1-4.

Table 1. Experiments in a simulated cobalt dichloride system.

No. crt.	Resin	Cobalt initial concentration, mg /L /pH	Breaking point		BV/h	Volume of the solution passed on the resin at saturation, mL/ Bed volumes
			Minutes	Bed volumes		
1	Purolite NRW 1600	447,82/ 5	720	47.17	4.88	3525/ 283,02
2	Purolite NRW 1600	240,32/2	180	31,45	9,41	4400/345,91
3	Purolite NRW 1600	242,43/5	180	31,45	9,41	4400/345,91
4	Purolite NRW 1600	242,43/5	182	31,45	10,27	4600/361,64

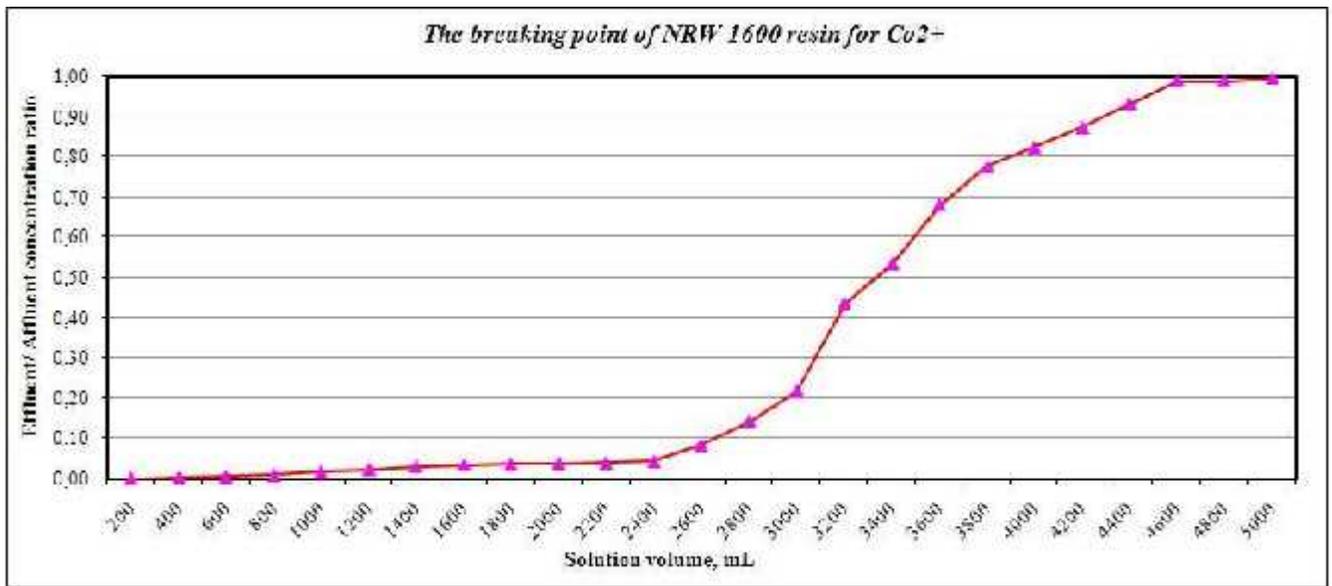


Figure 1. Curba de str. pungere a r. inii NRW1600 la reținerea Co^{2+} în funcție de volumul soluției ($C_0 Co^{2+} = 242,43$ mg/L, Volum r. in = $12,72$ cm³, pH=5,00) *The breaking curve of NRW 1600 resin for Co^{2+} versus solution volume ($C_0 Co^{2+} = 242.43$ mg/L, Resin volume = 12.72 cm³, pH=5.00)*

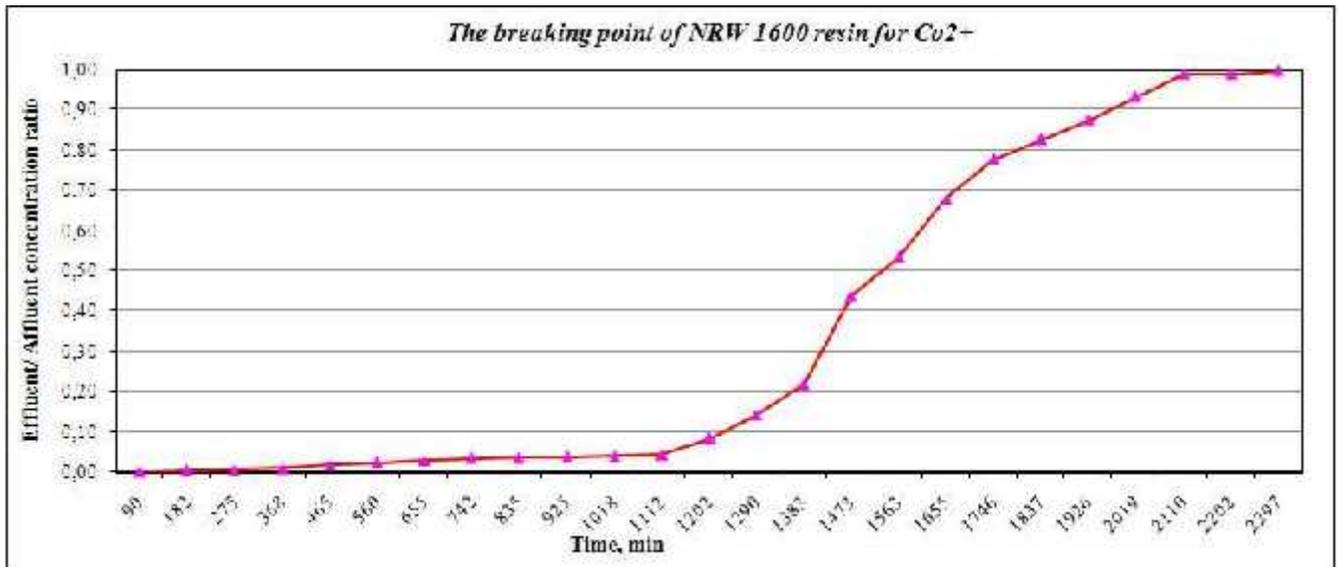


Figure 2. Curba de str. pungere a r. inii NRW1600 la reținerea Co^{2+} în funcție de timp ($C_0 Co^{2+} = 242,43$ mg/L, Volum r. in = $12,72$ cm³, pH=5,00) *The breaking curve of NRW 1600 resin for Co^{2+} versus time ($C_0 Co^{2+} = 242.43$ mg/L, Resin volume = 12.72 cm³, pH=5.00)*

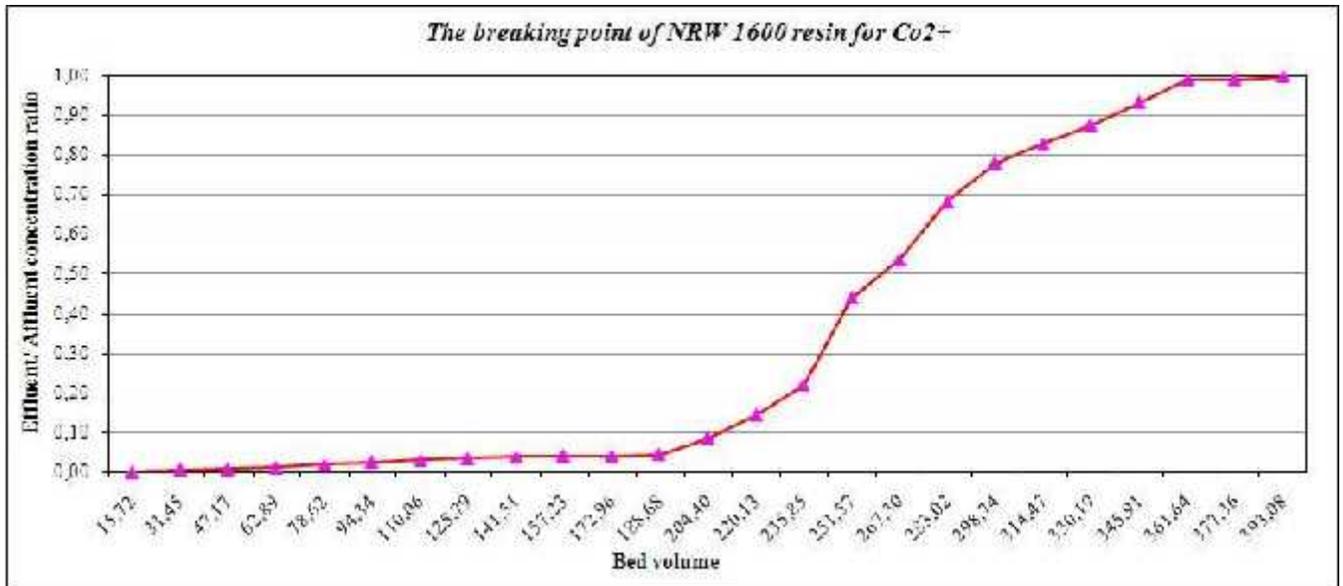


Figure 3. Curba de str pungere a r inii NRW1600 la reținerea Co^{2+} în funcție de bed volume ($C_0 Co^{2+} = 242,43$ mg/L, Volum r in =12,72 cm^3 , pH=5,00) *The breaking curve of NRW 1600 resin for Co^{2+} versus bed volume ($C_0 Co^{2+} = 242.43$ mg/L, Resin volume =12.72 cm^3 , pH=5.00)*

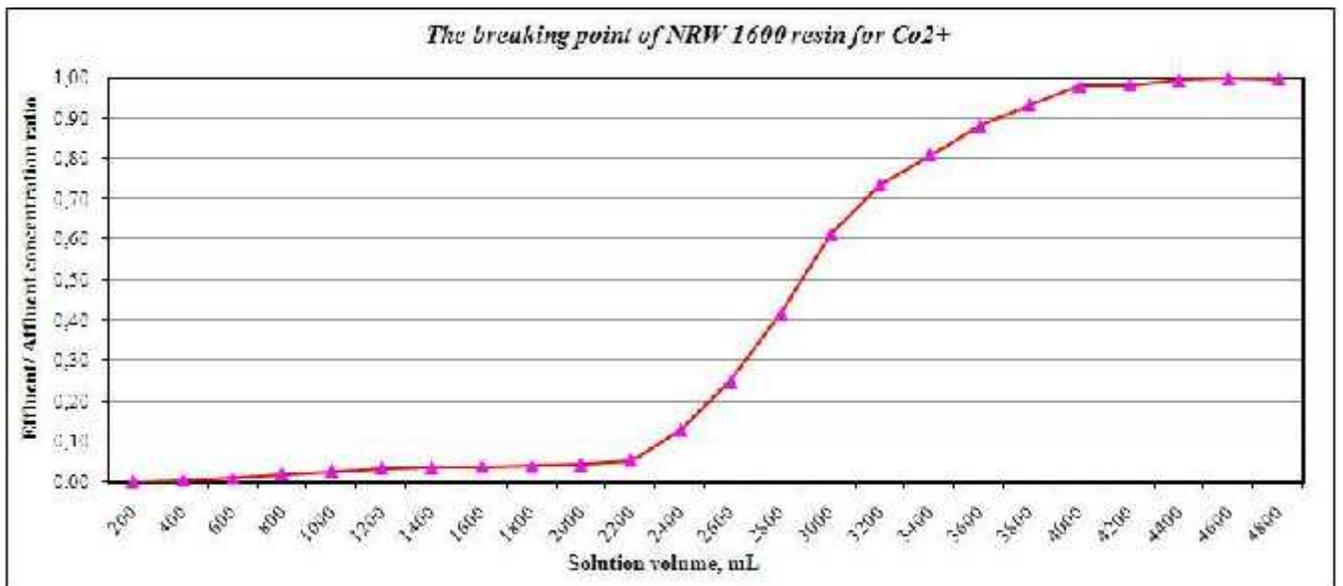


Figure 4. Curba de str pungere a r inii NRW1600 la reținerea Co^{2+} în funcție de volumul soluției ($C_0 Co^{2+} = 240,32$ mg/L, Volum r in =12,72 cm^3 , pH=2,00) *The breaking curve of NRW 1600 resin for Co^{2+} versus solution volume ($C_0 Co^{2+} = 240.32$ mg/L, Resin volume =12.72 cm^3 , pH=2.00)*

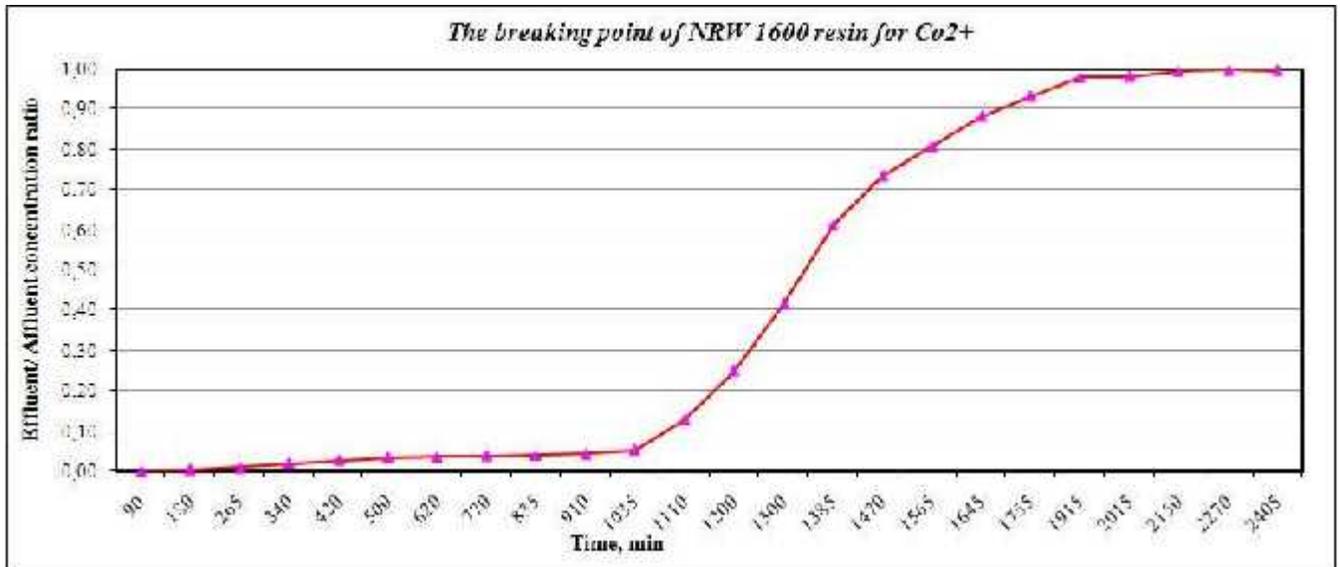


Figure 5. Curba de strângere a rîinii NRW1600 la reținerea Co^{2+} în funcție de timp ($C_0 \text{Co}^{2+} = 240,32 \text{ mg/L}$, Volum rîn = $12,72 \text{ cm}^3$, $\text{pH}=5,00$) *The breaking curve of NRW 1600 resin for Co^{2+} versus time ($C_0 \text{Co}^{2+} = 242.43 \text{ mg/L}$, Resin volume = 12.72 cm^3 , $\text{pH}=2.00$)*

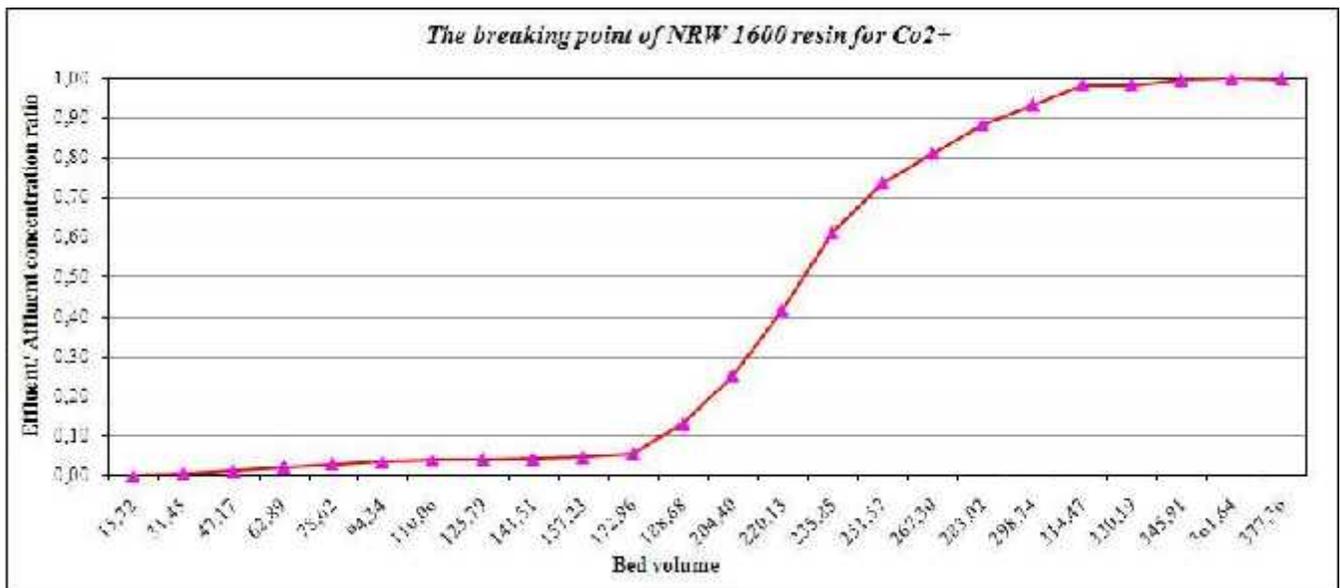


Figure 6. Curba de strângere a rîinii NRW1600 la reținerea Co^{2+} în funcție de bed volume ($C_0 \text{Co}^{2+} = 240,32 \text{ mg/L}$, Volum rîn = $12,72 \text{ cm}^3$, $\text{pH}=2,00$) *The breaking curve of NRW 1600 resin for Co^{2+} versus bed volume ($C_0 \text{Co}^{2+} = 240.32 \text{ mg/L}$, Resin volume = 12.72 cm^3 , $\text{pH}=2.00$)*

The experiments revealed that the pH value does not affect breakthrough curve crossing the resin NRW1600 CoCl_2 solutions.

Changes in the curve occurs with variation in initial concentration of cobalt, and flow. Thus, at a rate of two times less than a double concentration initial Co²⁺, the breaking occurs after 720 min. of a solution of CoCl₂ and the point of saturation to 3600 ml of a solution of CoCl₂, to 180 min. and 4600 mL saturation point CoCl₂ for more diluted solution.

3. Experimental works performed at ICN

The purpose of the work was the assessment of the treating and conditioning technology of the organic liquid radioactive waste (oil) from Cernavoda NPP. This was conducted in two phases:

- Phase I was conducted with two bench tests with providing acceptable decontamination agents of the oil waste- as see in previous tests, presented in TECHNICAL REPORT issued in 2014;
- Phase II involved paint filter testing and its performance (incinerability, heat release and tritium exposure hazard) of the solidified material.

The technology assessment for solidification of large variety of organic radioactive waste was conducted in the following bench-scale tests aimed to determine the performance of the solidification agents selected:

- Test no. 3 - Absorption of the organic and aqueous waste in order to meet Paint Filter Test Requirements (EPA 9095);
- Test no. 4 - Evaluation of the incinerability of the solidified product;
- Test no.5 - Determination of the heat release during solidification process;
- Test no.6 - Determination of the tritium exposure hazard due to solidified product.

The types of the two pairs absorbent polymers were used in the tests:

- Waste Lock® 770 and OrganoLock™ N-65
- Nochar N910 and Petrobond®.

Experimental tests and results

The bench-scale tests 3÷6 were conducted in the radioactive section of the laboratory. The personnel involved in performing the experimental tests wear the appropriate personal protective equipment. The personal protective equipment consisted

of one pair of disposable coveralls, cotton glove liners, rubber gloves (reusable) and plastic shoe covers the booties. No respiratory equipment was required during demonstration operations. A tritium monitoring equipment was in service while all experimental tests were performed. Radioactive laboratory hoods were used for the bench tests performed in the laboratory. All waste resulted from experiments were handled and disposed of according to the RATEN-ICN waste management plan.

Test no.3-Absorption of the organic and aqueous waste in order to meet Paint Filter Test Requirements (EPA 9095)

The tests are aimed to determine the performances of the absorbent polymers for solidify of the organic and aqueous waste in order to meet Paint Filter Test Requirements (EPA 9095). The tests were performed to estimate the compatibility of polymers to waste and assess ratios on case by case the absorbency ratio (g/g) and increase in volume factor (ml/ml) of the solidification products.

To conduct the experiments the necessary items included: glass beakers, glass stirrer, absorbent polymers, real /simulant waste and a weight scale.

To compensate the water content, the Waste Lock® or Nochar® A660 product was added to OrganoLock™ N-65 or to NOCHAR® A-610 respectively, at a specific percentage of the total solidification agent weight by weight to solidify the oil waste (20%) and Liquid Scintillation cocktail (65%). After the oil/water waste was pre-weighed, to obtain the proper Absorbency Ratio, the following ways was used for the preparation of the samples bench-scale test no. 3:

- Waste added gradually to the polymer absorbent. No stir;
- Waste added step-by-step in 4 layered approach;
- Waste added gradually to the polymer absorbents with gentle stirring;
- Polymer absorbents added gradually to the waste with gentle stirring.

Figure 7 present the Flow chart for determine the performance of the solidification agents for organic liquid waste in compliance with EPA 9095B method.

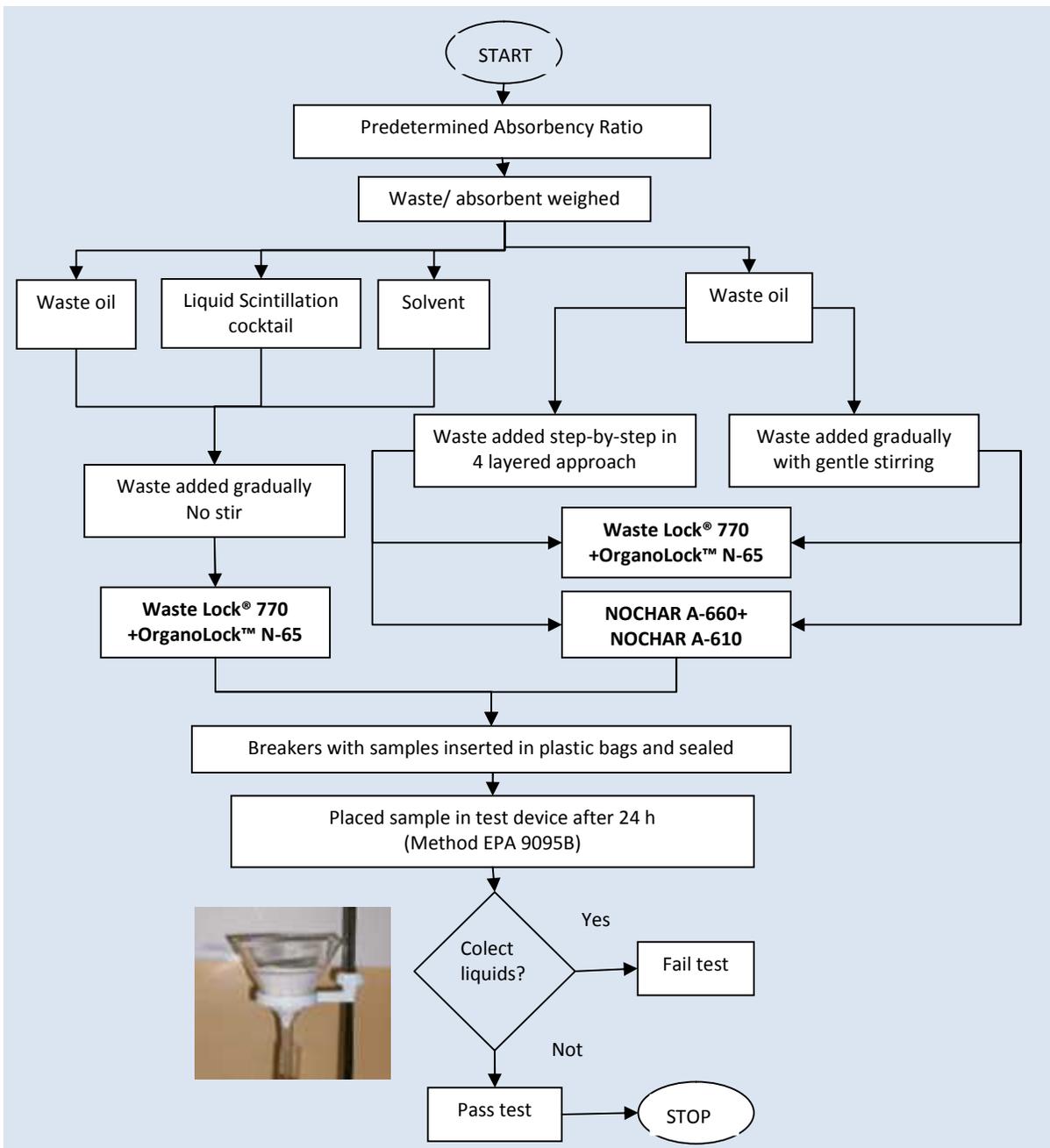


Figure 7. Flow chart for determination the performance of the solidification agents for the organic waste in compliance with EPA 9095B method

The entire amounts were resulted from each category of organic liquid radioactive waste solidify according to the flow charts presented in figure 1 for determination the presence / absence of free liquid, according to EPA Method 9095B. The results for bench-scale tests are show in Table 2.

Table 2. Data results of the bench-scale Test no.3-Absorption of the organic liquid waste

Sample No.	Waste type	Solidification agent type	Remarks	Absorbency Ratio (gram/gram)	Results Test Pass/Fail
1	Oil	Waste Lock® 770(20%) +OrganoLock™ N-65(80%)	Waste added gradually to the polymer absorbents. No stir	3	Fail
2	Oil	Waste Lock® 770(20%) +OrganoLock™ N-65(80%)	Waste added step-by-step in 4 layered approach	2,2	Pass
3	Liquid Scintillation cocktail	Waste Lock® 770(65%) +OrganoLock™ N-65(35%)	Waste added step-by-step in 4 layered approach	3	Fail
4	Liquid Scintillation cocktail	Waste Lock® 770(65%) +OrganoLock™ N-65(35%)	Waste added step-by-step in 4 layered approach	2,2	Pass
5	Solvent	Waste Lock® 770(20%) +OrganoLock™ N-65 (80%)	Waste added step-by-step in 4 layered approach	4	Fail
6	Solvent	Waste Lock® 770(20%) +OrganoLock™ N-65 (80%)	Waste added step-by-step in 4 layered approach	3,8	Pass
7	Oil	Waste Lock® 770(20%) +OrganoLock™ N-65 (80%)	Waste added step-by-step in 4 layered approach	2,2	Pass
8	Oil	Waste Lock® 770(20%) +OrganoLock™ N-65(80%)	Waste added gradually to the polymer absorbents with gentle stirring	2,2	Pass
9	Oil	NOCHAR A-660(20%)+ NOCHAR A-610(80%)	Waste added step-by-step in 4 layered approach	2,2	Pass
10	Oil	NOCHAR A-660(20%)+	Waste added gradually to the	2,2	Pass

		NOCHAR A-610(80%)	polymer absorbents with gentle stirring		
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Some images taken during experiments performed to determine the absorption of the organic waste are presented in figure 8 and 9.

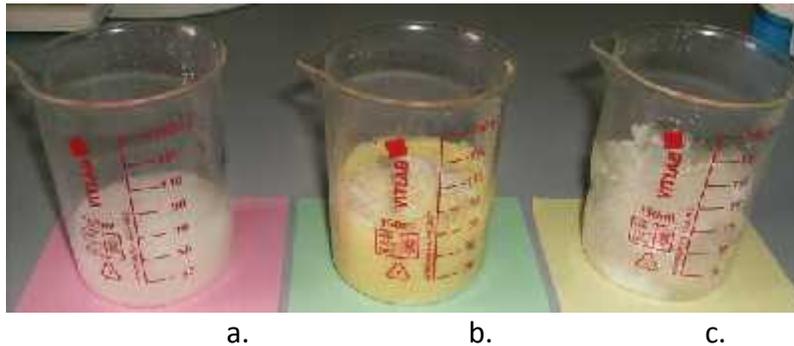


Figure 8. The bench-scale test no.3 performed to determine the absorption of the organic waste.

Waste added gradually with gentle stirring (a-Liquid Scintillation cocktail, b-Oil, c-Solvent)

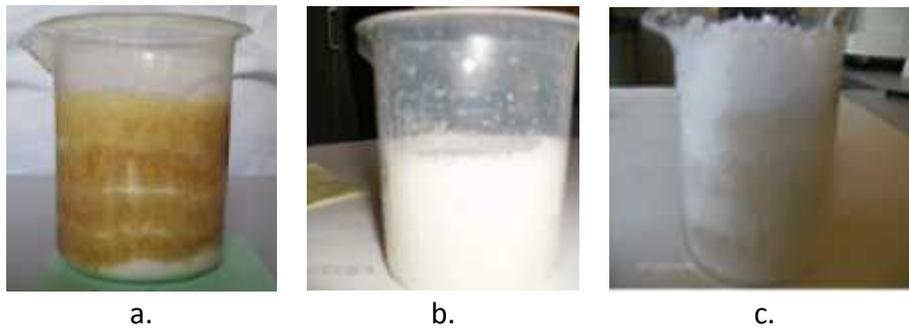


Figure 9. The bench-scale test no.3 performed to determine the absorption of the organic waste.

Waste added step-by-step in 4 layered approaches (a- Oil, b- Liquid Scintillation cocktail, c- Solvent)

Test no.4 - Evaluation of the incinerability of the solidified product

The test no. 4 should prove whether the absorbent polymers OrganoLock™ N-65 and / or Waste Lock® 770 might be used for embedding liquid radioactive waste from Cernavoda NPP and the products are suitable for incineration, resulting in a small ash percentage.

The tests for evaluation of the incinerability of the solidification product from small-scale tests were focused on the establishing how readily the material ignites, smoke evolution and the amount of the resulted ash.

Bench-scale demonstration was conducted in the radioactive section of the laboratory. There were conducted three rounds of testing using 0,5 g of the samples of each category of the solidified waste (liquid scintillation cocktail and oil to comply with the table 1) and 0.5 g of the couple of absorbent polymers (ORGANOLOCK™ N-65 and WASTE LOCK® 770).

Flow chart for predicting the incinerating capacity of the solidified product is presented in figure 10.

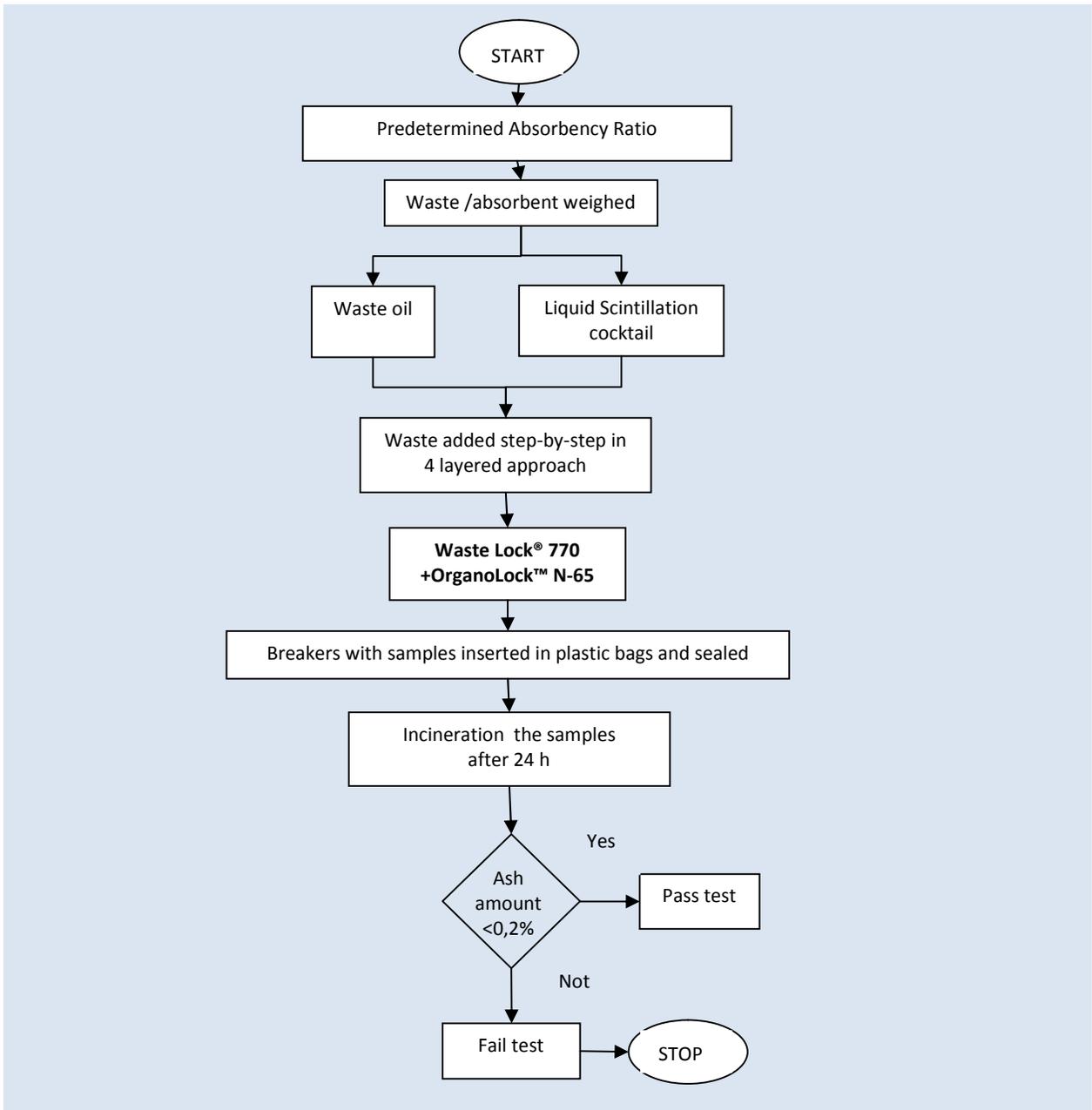


Figure 10. Flow chart for predicting the incinerating capacity of the solidified product

The absorbent polymers, if subjected to some suitable ignition sources, will undergo self-sustained combustion in air. They are burning with flaming combustion.

Below 350°C, the absorbent polymers melted quickly, with visible vapour and gases as it is shown in Figure 11.

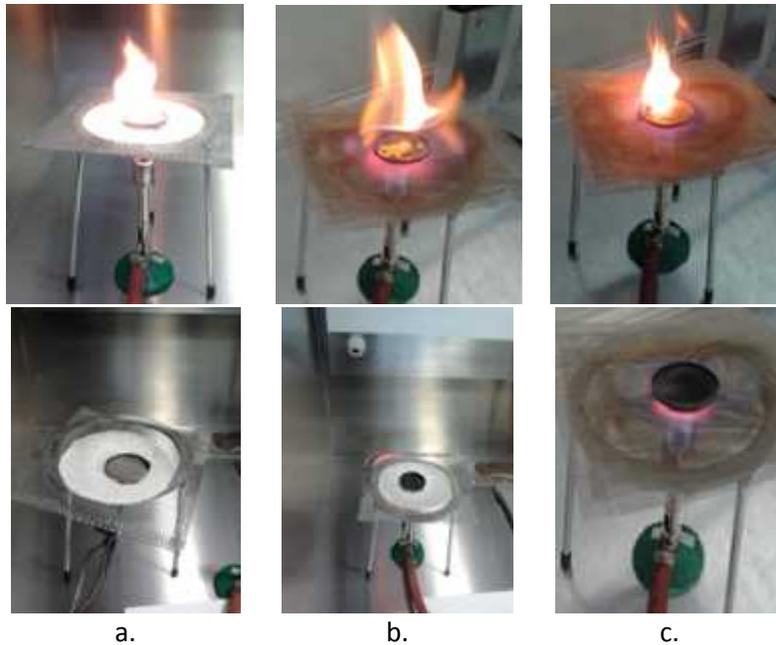


Figure 11. Sample tests after 1-3 minutes to start incineration tests(a- ORGANOLOCK™N-65+WASTE LOCK® 770, b- Liquid Scintillation cocktail+ ORGANOLOCK™N-65+ WASTE LOCK® 770, c- Oil + ORGANOLOCK™N-65+WASTE LOCK® 770)

The results of tests for evaluation of the incinerability of the solidified product show that the selected solidification agents (ORGANOLOCK™ N-65 and 770 WASTE LOCK®) can be incinerated, resulting in a small ash percentage (less than 0.2%).

Test no. 5 - Determination of the heat release during solidification process

Solidified waste forms will be packaged and storage for transport to incineration facility. The bench-scale tests should prove whether the absorbent polymers OrganoLock™ N-65 and / or Waste Lock® 770 during the solidification process of the organic radioactive waste are releasing heat.

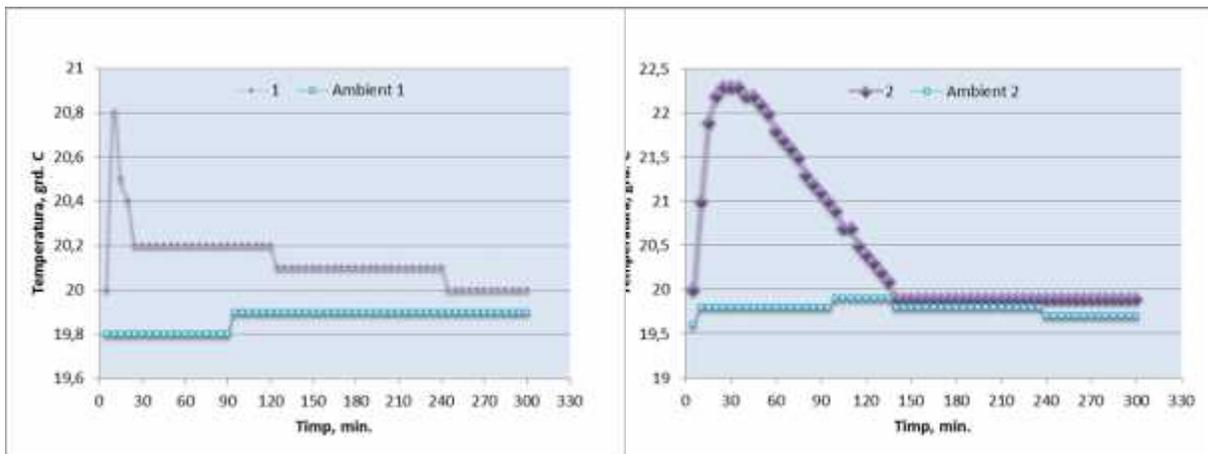
There were performed two rounds of tests in view of determining the heat release for the samples of the oil waste and the liquid scintillation cocktail solidified with the pair absorbent polymers.

The beakers with the samples are placed in a thermally insulated chamber, equipped with a recording thermometer, according to Figure 12.



Figure 12. Samples before / after the introduction inside the thermally insulated chamber

The data temperature was recorded in the calorimeter during the absorption of liquid organic radioactive waste (figure 13).



a. Oil+ORGANOLOCK™N-65+WASTE b. Scintillation cocktail+ORGANOLOCK™N-65+WASTE LOCK®

Figure 13. The temperature recorded during solidification of the organic waste

The temperature recorded during the solidification process of the organic liquid waste with the selected absorbent polymers increases with $1\div 2.5^{\circ}\text{C}$ in the first $15\div 30$ minutes, depending on the waste type.

Test no.6 - Determination of the tritium exposure hazard due to solidified product

Power plant operators will generally have procedures for allocation of acceptable risk and radiation exposure across different operations on the same site. The introduction of new waste treatment processes must be considered against these risk and dose levels, and this may have an impact on the selection of technology.

The tritium exposure hazard associated with the solidification products of the two couples of absorbent polymers comply with the requirements of the national regulations concerning radioactive waste management activities. It is considered the following workers protection regulations:

- The annual limit of incorporation from tritium (LAIH-3) representing work by an occupationally exposed worker exposed to a dose of 20 mSv in accordance with NDR-04 is $1,00E+09$ Bq;
- Derived air concentration (CDA) of a radionuclide representing the tritium activity concentration in air for a person which works for 8 hours every day for 5 days weekly and 50 weeks yearly = 2000 hours is:

$$CDA = 1,00E+09 / 2000 \times 1,2 = 4,17E+05 \text{ Bq/m}^3$$

- Effective dose limit (D) for occupationally exposed workers is $20 \text{ mSv/year} = 0,01 \text{ mSv/h} = 10 \mu\text{Sv/h}$
- Conversion factor for $1 \mu\text{Sv/h}$ (F) is:

$$F = CDA / D = 41,7 \text{ Bq/l}$$

- Concentration equivalent is 208 Bq/l for a conservative criterion for a $5 \mu\text{Sv/h}$.

The bench-scale tests were performed to estimate the tritium effective dose rate of the solidified product. The tests are conducted using 165 g of the samples of each category of waste absorbed tested. For each category of waste it was used two methods for absorption (stratification and gentle mix the polymer absorbents), different specific activity of tritium in the waste ($2,8E+05 \text{ Bq/kg}$ to $1,50E+07 \text{ Bq/kg}$), and different absorbent capacity (2,2-3).

Flow chart for determination of the tritium exposure hazard due to solidification process is presented in figure 14.

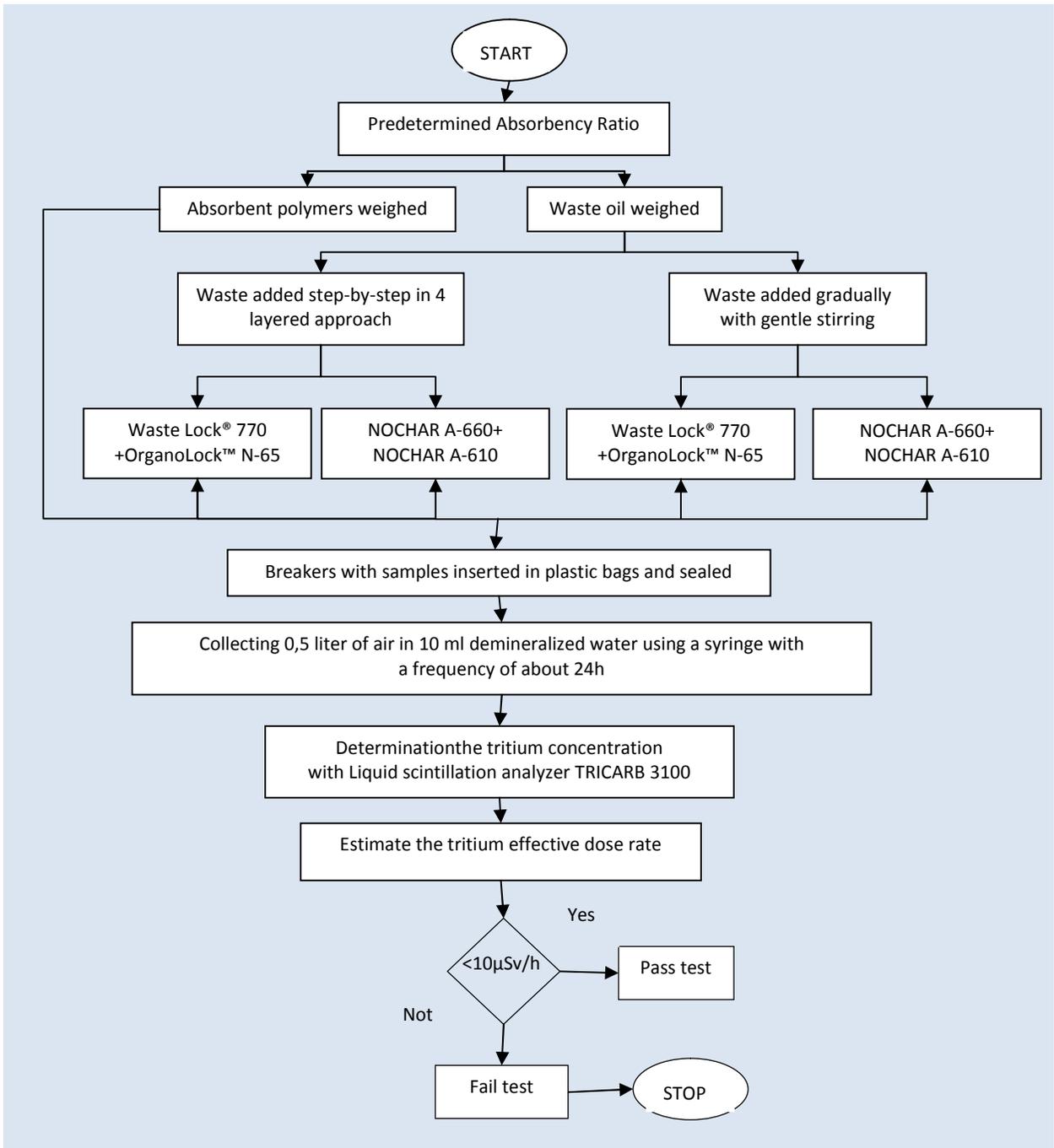


Figure 14. Flow chart for determination of the tritium exposure hazard due to oil solidification

Data results of the bench-scale Test 6 to estimate the tritium effective dose rate of the oil waste solidify with absorbent polymers is given in table 3.

Table 3. Data results of the bench-scale Test no.6. Estimation of the tritium effective dose rate of the oil waste solidify with absorbent polymers

Test No	Absorbent type	Absorption mode	Absorbent capacity (w/w)	Tritium concentration in waste, Bq/kg	Effective dose rate, $\mu\text{Sv/h}$				Results Test Pass/Fail
					Time, h				
					24	48	72	96	
1	Waste Lock® 770(20%)+Organolock™ N-65(80%)	Waste added step-by-step in 4 layered approach	2,2	2,8E+05	1,39	0,87	0,81	0,71	Pass
2	Waste Lock® 770(20%)+Organolock™ N-65(80%)	Waste added step-by-step in 4 layered approach	3	2,8E+05	1,34	0,98	0,77	0,81	Pass
3	NOCHAR A-660(20%)+NOCHAR A-610(80%)	Waste added step-by-step in 4 layered approach	2,2	2,8E+05	0,52	0,46	0,41	0,41	Pass
4	NOCHAR A-660(20%)+NOCHAR A-610(80%)	Waste added step-by-step in 4 layered approach	3	2,8E+05	0,61	0,46	0,42	0,35	Pass
5	Waste Lock® 770(20%)+Organolock™ N-65(80%)	Waste added step-by-step in 4 layered approach	2,5	2,07E+06	17,64	N/A	16,45	17,61	Fail
6	Waste Lock® 770(20%)+Organolock™ N-65(80%)	Polymer added gradually to waste with gentle stirring	2,5	1,50E+07	28,17	N/A	21,99	24,13	Fail

Conclusion

Assessment of the treatment and conditioning technology of organic liquid radioactive waste supported by tests in the laboratory on a small volume of real samples from the Cernavoda NPP carried out by specialists from RATEN ICN Pitesti from the implementation team of the project, allow to draw the following conclusions:

- The absorbent polymers are used in treatment of a large variety of organic liquid waste (waste water, oil, solvent, liquid scintillation cocktail). Reasonable results were obtained with the investigated absorbent polymers.
- The results of Paint Filter Test (EPA 9095) show that the selected solidification agents are suitable for the proposed goal. The polymers have an absorbent capacity over 2 (w/w) with a minimal volume increasing.
- The best mode of doing absorption is to solidify the radioactive waste in small batches. The absorbent capacity of the absorbent polymers used in the most type of the waste isn't depend of the ways of the preparation of the samples in the bench-scale test 3. Slow and short-term mixing was required at the absorbency ratio between 2 and 3. The absorbency ratio of 2,2 is the limit for an acceptable and safe solidification for oil. For an acceptable and safe solidification waste water the limit of the absorbency ratio is 3. The absorbency ratios offer economic advantages to waste generators (Cernavoda NPP).
- Packaged in containers, the solidified waste with absorbent polymers (Waste Lock® 770 and OrganoLock™ N-65) can be safely stored and transported without the possibility of tritium leaching by evaporation;
- The solidification product for the type of organic waste tested with solidification agents (ORGANOLOCK™ N-65 and 770 WASTE LOCK®) can be incinerated, resulting in a small ash percentage (less than 0,2%).
- The tritium exposure hazard associated with the solidification products of the pair of absorbent polymers complies with the requirements of the national regulations concerning radioactive waste management activities. The both pairs of absorbent polymers have similar comportment for the absorbent ratio below 2,2 for oil and 3 for water waste and not depend of absorption mode. Immobilization using the pair of absorbent polymers (ORGANOLOCK™ N-65 and WASTE LOCK® 770) and storage of products after solidification is safe for the oil waste with Tritium specific activity below $2,4E+06\text{Bq/kg}$. For more Tritium specific activity it is necessarily previous decontamination step established in the bench-scale tests 1÷2.

4. Theoretical basis of the equipment necessary for application of the technology.

Experimental work presented in previous reports doubled by the mathematical modeling work offer important information concerning the equipment type recommended to be used in the industrial process, the materials used and the scale-up procedure.

First of all, an overview about the wastewater treatment technology improvement implies a first step with estimation of the strategy to be followed in the equipment designing. Two important ways could be imagined: one linked to small storage capacities and low processing installations capacities (that way imply low investment costs but probably high operating costs versus other way) and the second one implying high storage capacities of the contaminated wastewater doubled by high processing installation capacities. Obvious, since we talk about wastewater contaminated with some radionuclide it is preferable to diminish to maximum possible the residence time of the radionuclide in the industrial plant (with respect to the safety or specific laws for nuclear activity plants – linked with wastewater treatment). That means a fast water treatment; the recovery of important species and the water recycle in the system. But our recommendation is to take a decision about the wastewater treatment capacity in accordance with available data concerning the wastewaters quantities in time available from the industrial plant. So not only technical and safety reasons should be considered but also economical criterion should be taken into account.

Applying the results given by the experimental and theoretical research means to follow two steps: the scale-up laboratory devices and the detailed designing of all industrial devices needed in the wastewater treatment plant.

A start-up point of scale-up activity it should be the conception of the technological scheme (at industrial scale). Some devices (like storage vessels, pumps, pipes) are not present during the laboratory experiments. So a first draft of a possible technological scheme (with possible options) will give a first image of this issue. A secondary path of the installation, designated to the resin change in the system obviously should be considerate and also the periodically clean-up of all devices and pipes.

The considered **storage vessel** capacity should be in accordance with the wastewater input accounted and the installation treatment capacity. Also, another important point linked to this device should be the mixing device of the storage tank. Since the experimental work at laboratory scale is done at constant concentration of the radionuclide in the input wastewater, the same procedure should be applied at industrial scale. Any sedimentation process that could occur during the storage time (between two processing periods) must be eliminated. A simple mechanical stirring device or a recycle path of the wastewater from the used pump for column feeding could be considered. The storage vessel could be considered in two situations:

- **Atmospheric Tanks** The term *atmospheric tank* as used here applies to any tank that is designed to be used within plus or minus several hundred Pascals of atmospheric pressure. It may be either open to the atmosphere or enclosed. Minimum cost is usually obtained with a vertical cylindrical shape and a relatively flat bottom at ground level.

- **Elevated Tanks** These can supply a large flow when required, but pump capacities need be only for average flow. Thus, they may save on pump and piping investment. They also provide flow after pump failure, an important consideration for fire systems.

Calculation of Tank Volume. A tank may be a single geometrical element, such as a cylinder, a sphere, or an ellipsoid. It may also have a compound form, such as a cylinder with hemispherical ends or a combination of a toroid and a sphere. Each geometrical element of the tank usually must be calculated separately to establish the total volume. Calculations for a full tank are usually simple, but calculations for partially filled tanks may be complicated.

In the case of a **partially filled horizontal cylinder** refer to Fig.15

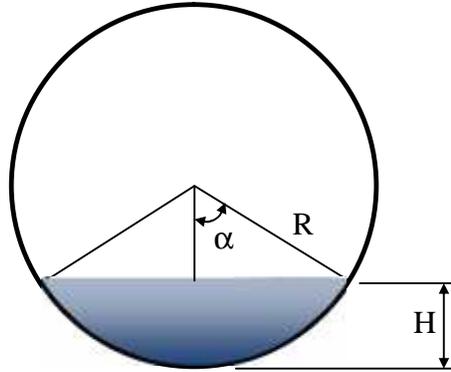


Figure 15. Volume of partially filled horizontal tanks calculation. H = depth of liquid; R = radius; D = diameter; L = length; α = half of the included angle; and $\cos \alpha = 1 - H/R = 1 - 2H/D$.

The angle α is calculate in degrees. Any units of length can be used, but they must be the same for H , R , and L . The liquid volume will be:

$$V = L \cdot R^2 \cdot \left(\frac{\alpha}{57.30} - \sin \alpha \cdot \cos \alpha \right) \quad (1)$$

This formula may be used for any depth of liquid between zero and the full tank, provided the algebraic signs are observed. If H is greater than R , $\sin \alpha \cdot \cos \alpha$ will be negative and thus will add numerically to $\alpha/57.30$. The **volumes of heads** must be calculated separately and added to the volume of the cylindrical portion of the tank. The four types of heads most frequently used are the standard dished head, torispherical head, ellipsoidal head, and hemispherical head. A partially filled horizontal tank requires the determination of the partial volume of the heads. A formula for partially filled heads is [4]:

$$V = 0.215 \cdot H^2 \cdot (3 \cdot R - H) \quad (2)$$

where V = volume, R = radius, and H = depth of liquid. Some simplifying assumptions which affect the volume given by the equation are made in literature, but the equation is satisfactory for determining the volume as a fraction of the entire head.

Container Materials and Safety. As it is known, storage tanks are made of almost any structural material. Steel and reinforced concrete are most widely used. Plastics and glass-reinforced plastics are used for tanks up to about 230 m³. Resistance to corrosion, light weight, and lower cost are their advantages. Plastic and glass coatings are also applied to steel tanks. Nonferrous metals are used only when their special properties are required. When expensive metals such as tantalum are required, they may be applied as tank linings or as clad metals. Small tanks containing nontoxic substances are not particularly hazardous and can tolerate a reduced factor of safety. Tanks containing highly toxic substances and very large tanks containing any substance can be hazardous. The designer must consider the magnitude of the hazard. The possibility of brittle behavior of ferrous metal should be taken into account in specifying materials. The container material chooses should respect all rules imposed by the nuclear industry. Also if clean-up process during periodically revisions implies the use of strong acids or basic solutions that should influence the container material choose.

Pump selection. Selecting pumps for any service imply the necessity a lot of data about the liquid to be handled, the total dynamic head, the suction and discharge heads, and, in most cases, the temperature, viscosity, vapor pressure, and specific gravity. The task of pump selection is frequently further complicated by the presence of solids in the liquid and liquid corrosion characteristics requiring special materials of construction. Solids may accelerate erosion and corrosion, have a tendency to agglomerate, or require delicate handling to prevent undesirable degradation. Since radioactive liquids are involved in transport procedure a solution in pump selection could be choose a kinetic special pump [4] gas lift type to reduce the nuclear contamination of the device.

Range of operation. Because of the wide variety of pump types and the number of factors which determine the selection of any one type for a specific installation, the designer must first eliminate all but those types of reasonable possibility.

Pump Materials of Construction In the chemical industry, the selection of pump materials of construction is dictated by considerations of corrosion, erosion,

personnel safety, and liquid contamination. The experience of pump manufacturers is often valuable in selecting materials.

Presence of solids. If a liquid containing suspended solids, must be transported there are unique requirements which must be considered. Adequate clear-liquid hydraulic performance and the use of carefully selected materials of construction may not be all that is required for satisfactory pump selection. Dimensions of all internal passages are critical. Must be avoided pockets and dead spots, areas where solids can accumulate. Close internal clearances are undesirable because of abrasion. Flushing connections for continuous or intermittent use should be provided. Chemical pump installations that require annual maintenance costing 2 or 3 times the original investment are not uncommon. In most cases this expense is the result of improper selection [4].

Concerning the **ion exchange column**, data about the ion exchange recommended resin were above mentioned. Some theoretical considerations are useful for the scale-up activity.

Ion exchangers classification. Ion exchangers are classified according to (1) their functionality and (2) the physical properties of the support matrix. Cation and anion exchangers are classified in terms of their ability to exchange positively or negatively charged species. Strongly acidic and strongly basic ion exchangers are ionized and thus are effective at nearly all pH values (pH 0–14). Weakly acidic exchangers are typically effective in the range of pH 5–14. Weakly basic resins are effective in the range of pH 0–9. Weakly acidic and weakly basic exchangers are often easier to regenerate, but leakage due to incomplete exchange may occur [4].

Except in very small-scale applications, ion-exchangers are used generally in cyclic operations involving sorption and desorption steps. A typical ion-exchange cycle for water-treatment applications involves (a) *backwash*—used to remove accumulated solids obtained by an upflow of water to expand (50–80 percent expansion is typical) and fluidize the exchanger bed; (b) *regeneration*—a regenerant is passed slowly through the used to restore the original ionic form of the exchanger; (c) *rinse*—water is passed through the bed to remove regenerant from the void volume and, in the case of porous exchangers, from the resin pores; (d) *loading*—the fresh solution to be treated is passed through the bed until leakage begins to occur.

A complete deionization with ion-exchange columns is the classical method of producing ultrapure water for boiler feed, in electronics manufacture, and for other general uses in the chemical and allied industries. For deionization will be necessary two exchangers with opposite functionality to remove both cations and anions. These can be in separate columns, packed in adjacent layers in the same column, or, more frequently, in a mixed bed. In the mixed bed case, the two exchangers are intimately mixed during the loading step. For regeneration, backwashing separates the usually lighter anion exchanger from the usually denser cation exchanger. The column typically has a screened distributor at the interface between the two exchangers, so that they may be separately regenerated without removing them from the column. Differences in selectivity for different species can be used to carry out separations during the displacement [5] Multibed cycles are also used to facilitate integration with other chemical process operations.

General Design of the ion exchange devices.

A typical fixed-bed ion exchanger consists of a vertical cylindrical vessel of lined steel or stainless steel. Linings are usually of natural or synthetic rubber. Spargers are provided at the top and bottom, and frequently a separate distributor is used for the regenerant solution (if case). The resin bed, consisting of a meter or more of ion-exchange particles, is supported by the screen of the bottom distributor.

Externally, the unit is provided with a valve manifold to permit downflow loading, upflow backwash, regeneration, and rinsing. For deionization, a two exchanger assembly comprising a cation and an anion exchanger, is a common configuration . Characteristic design calculations are presented and illustrated by Applebaum [4]. Large amounts of data are available in published literature and in bulletins of manufacturers of ion exchangers. In general, however, laboratory testing and pilot-plant work is advisable to determine usable exchanger capacities, regenerant quantities, exchanger life, and quality of product for any application not already thoroughly proven in other plants for similar conditions [4]. For larger-scale applications, a number of continuous or semi continuous ion-exchange units are also available. The Higgins contactor was originally developed to recover uranium from leach slurries at the Oak Ridge National Laboratory

[4]. More recently, it has been adapted to a wide variety of applications, including large-volume water softening. The Asahi process [4] is used principally for high-volume water treatment.

Another continuous ion-exchange system is described by Himsley and Farkas [4]. Such a system is used to treat 1590 m³/h of uranium-bearing copper leach liquor using fiberglass- construction columns 3.7 m in diameter. The adsorption column is divided vertically into stages. Continuous transfer of batches of resin occurs from stage to stage without any interruption of flow. This is accomplished by pumping solution from one stage (A) to the stage (B) immediately above by means of external pumping in such a manner that the net flow through stage B is downward, carrying with it all of the resin in that stage B. When transfer of the ion exchanger is complete, the resin in stage C above is transferred downward in a similar manner. The process continues until the last stage (F) is empty.

General considerations about column scale-up. Sometimes passing from laboratory scale to industrial scale is a difficult step. The scale-up procedure should take into account various aspects concerning the process and corresponding devices. The main recommendation about this are presented further.

There are many different aspects related to scale-up, some of them technical and others not.

Economical aspect

Financially seen it looks more attractive to build one big apparatus rather than several parallel ones. The investment costs (Inv) go up with the production capacity (Cap) and for this it holds roughly the 0.6-rule for process equipment:

$$\text{Inv} \sim \text{Cap}^{0.6}$$

This can be simply seen by realising that $\text{Inv} \sim A$ (surface area of equipment) $\sim L^2$ and $\text{Cap} \sim V$ (volume of equipment) $\sim L^3$. From these two it follows $\text{Inv} \sim \text{Cap}^{2/3}$.

The exponent 2/3 is called the degression coefficient and changes from case to case. As long as the degression coefficient is smaller than unity there is an economic

incentive to increase the size of equipment rather than to multiply the equipment. The degression coefficient depends, of course, on the type of equipment. Also the effect of 'standard' sizes is important here. If, for example, a valve is made in different standard sizes than it could be cheaper to buy two smaller ones than to have a large one especially made.

General aspects of scale-up. The main aspects involved in scale-up activity are:

- Economical aspects (as it was already mentioned):

$$I \sim C^{0.6}$$

$$I \sim A \text{ (area)}$$

$$C \sim V \text{ (volume)}$$

- Energy, raw materials, and environment
- Vulnerability of the production to:
 - Maintenance
 - Sabotage
- Logistics:
 - Transportation of parts
 - Supply of raw materials
 - Discharge of products
- Social aspects:
 - Employability, labor conditions
- Mechanical and other technical restrictions
- Start-up, management, maintenance of a plant
- Safety

Scale-up considerations. The scale-up of the installation could be made in two ways: multiplying the number of pilot scale installation (**by number**) or by devices size enlargement (**by size enlargement**).

The advantages and disadvantages of each option are briefly presented as follows:

by number:

- fast design procedure: gain of time
- limited chance on practical constraints
- easier construction: small mechanical problems
- good possibility of sub-maximal production
- easier repair/cleaning; cheaper spare parts
- logistical problems in terms of distribution
- extra risk problems due to interference

by size enlargement:

- slower design procedure: loss of time
- equipment limitations due to practical constraints
- construction problems: mechanical constraints
- limited possibility for sub-optimal production
- difficult repair; limitation in spare parts
- logistical problems in terms of large quantities
- risk problems due to bulk quantities

Similarity. In the process industry all kinds of physical and chemical processes take place which in principle can be described mathematically by means of momentum, heat, and mass balances. The resulting description is usually too complex to allow general analytical solutions. Although these coupled partial differential equations can be solved numerically after some computer time, the obtained solutions are very specific and hardly suitable for generalization and analysis. In such cases it might be useful to replace the straightforward process description by a comparative method in which the processes at two different scales (sizes) of the process equipment are compared. From the conditions for process similarity, scale-up criteria with respect to that equipment can then be derived. So scale-up is actually designing using “foreknowledge”; this foreknowledge

can be the result of laboratory experiments or experience with a similar industrial process, possibly at a different scale.

Two kinds of similarity are distinguished:

- *apparatus similarity*, in which the dimensions of the apparatus are being scaled-up with a common scale-up factor; afterwards it is analyzed what effect scale-up has on the processes in the apparatus.

- *process similarity*, in which a certain process variable (production, energy consumption) is being scaled-up out of process considerations. Process requirements (such as product quality) result at process similarity in demands for the dimensions of the apparatus. So now scale-up of the dimensions is secondary.

Process equipment companies that produce relatively simple equipment often prefer apparatus similarity for production reasons. Also, a series of similar apparatuses (such as pumps) 'looks' better. However, often only the original design of such a series of apparatuses may be optimal and some (much) of that quality has been sacrificed in case of the 'derived' apparatuses. This is (one of) the reason(s) why the scale-up factor is never chosen far from unity and is seldom bridging one decade. With more complex equipment and for whole production processes (factories) apparatus similarity is never considered and only process similarity is used. Therefore, from now on, the word similarity will be used in the meaning of 'process similarity'. It should be mentioned that similarity between model and prototype means that the deformation, flow, temperature and concentration profiles of model and prototype are congruent in dimensionless form.

There exist *more levels* of process similarity. Moreover, there is also a certain hierarchy; each underlying form of similarity assumes the presence of the one above. We distinguish them as: geometric similarity (*shape*), mechanical similarity s: static (mechanical) *deformation profiles* or d: dynamic (mechanical) similarity *velocity profiles*, t: thermal similarity *temperature profiles*, c: chemical similarity *concentration profiles*. To derive the conditions for the different levels of process similarity it should be used momentum, heat, and mass balances; these balances will be formulated such that the analogy between these three types of transport is maximal.

General conclusions about similarity are:

- At each level of process similarity it is possible to indicate the conditions: equal dimensionless numbers at M- and P-scale

- Soon the number of conditions is that large that these conditions can only be satisfied with a scale-up factor equal to one

- Fortunately not all dimensionless numbers are important at all scales

- A method is needed to determine which dimensionless groups are really important and which are allowed to vary (hopefully at a modest scale). *Regime analysis* provides such a method.

Finally: only seldom full process similarity is possible (or desirable). If full similarity is not possible then *partial process similarity* must be accepted. The dimensionless groups, which have to be kept constant at both scales, form together the *scale-up criterion*.

Regime analysis and scale-up criteria.

Attempts to scale a process *fully similar* often fail due to the large number of dimensionless groups that have to be kept constant. Reasons to partly give up full process similarity can be of :

- (1) mathematical,
- (2) technological or
- (3) economical nature.

In the first case the conditions, which constrain the system by keeping the dimensionless groups constant, are mathematically contradictory.

In the second case certain technological boundaries are exceeded (gas velocities near the speed of sound, vibrations near the characteristic frequencies, etc.).

In the third case the design is becoming too expensive (special design, extreme costs of transportation, high costs for foundations or safety).

In all cases it should give up full process similarity and have to be satisfied with *partial similarity*: not all dimensionless groups required for full similarity will show in the scale-up criterion, but some will and some do not. Clearly it is a problem of choice, entering the field of *regime analysis*.

Hydraulic considerations [6]

In literature there are some correlations for the evaluation of particle Peclet number Pe_p and liquid holdup %h (as a percentage of the total bed volume) for materials that are frequently used in adsorption and ion exchange systems

$$Pe_p = N \cdot Re_p^n$$

Where

N is 0.52 for upflow and 0.05 for downflow

n is -0.65 for upflow and 0.48 for downflow

Re_p is particle Reynolds number $Re_p = \frac{d_p \cdot u_s \cdot \rho}{\eta}$

where η is the dynamic viscosity of the liquid phase,

ρ – liquid density;

d_p – particle diameter;

u_s – superficial velocity.

$$\%h = 21 + 99.72 \cdot u_s^{0.28}$$

Liquid holdup equation holds for particle size of 1.2-1.3 mm. Then, the bed Peclet number can be evaluated using the following equation [Levenspiel O.(1972) Chemical Reaction Engineering, 2nd Ed., Wiley Eastern Limited]

$$Pe_L = Pe_p \cdot \frac{L}{d_p}$$

The dynamic liquid holdup can be evaluated for other particle diameters following the equation:

$$\frac{\%h(d_{p1})}{\%h(d_{p2})} \cong \left(\frac{d_{p2}}{d_{p1}} \right)^m$$

Where the exponent m is 0.72 [7,8]

The constant part in liquid holdup correlation (equal to 21) is the static liquid holdup. This part is between (0.11/) and (0.072/) for particle size between 0.2 and 2 mm, where ϵ is the bed voidage In the typical case of $\epsilon = 0.4-0.5$ static holdup is between 14 and 27% [6].

Several authors [9-11] precise that certain geometrical analogies should be kept within the following limits in order to avoid large-scale maldistribution of the flow

$$\frac{L}{D} \geq 5$$

$$\frac{D}{d_p} \geq 12 - 30$$

$$\frac{L}{d_p} \geq 50 - 150$$

where L is the bed length, D the bed diameter and d_p is the particle diameter.

Also, Ruthven [11] precises that a maximum linear velocity should not be exceeded in order to avoid extended friction between the packing material in both down and upflow operations. This velocity is 0.8 times the minimum fluidization velocity for upflow operation and 1.8 times the same velocity for downflow operation. Using this maximum working velocity and the contact time during pretreatment (which is generally higher than the treatment one) the maximum bed high could be determined as follows:

$$F_{FS} = a \cdot V_{FS}$$

where FS stands for “full scale”

F is the volumetric flow rate and V is the bed volume

The number a is the number of bed volume per hour.

$$u_{FS} = \frac{F_{FS}}{A_{FS}} = \frac{a \cdot V_{FS}}{A_{FS}} \leq u_{FS, \max}$$

A is the bed cross sectional area

u_{\max} is the maximum allowable linear velocity

Considering that $V_{FS} = A_{FS} \cdot L_{FS}$, it result that

$$L_{FS} \leq \frac{u_{FS,\max}}{a}$$

Could be used a bed with a length which represent 85 % off this value

Those considerations did not take into account the possible compression of the particles at the bottom of the bed, under the bed weight and under the hydrostatic pressure of the fluid

But Inglezakis [13] showed that the beds of 1.4 – 1.7 mm particle size can be very high (50 m).

Also, in Inglezakis et al. [6] is developed the following relation to estimate the full scale flow rate:

$$F_{FS} \leq (10 \cdot D_{LS})^2 \cdot \frac{a \cdot \pi \cdot L_{FS}}{4}$$

where LS stands for laboratory scale

The bed porosity should be the same. It is a function of D/d_p , but for d_p/D values (lower than 0.1) it is practically constant.

MAINTAINING FLUID FLOW IN PIPING SYSTEMS

The primary purpose of any piping system is to maintain free and smooth flow of fluids through the system. Another purpose is to ensure that the fluids being conveyed are kept in good condition (i.e., free of contamination). Piping systems are purposely designed to ensure free and smooth flow of fluids throughout the system, but additional system components are often included to ensure that fluid quality is maintained. Piping system filters are one example, and strainers and traps are two others. It is extremely important to maintain free and smooth flow and fluid quality in piping systems, especially those that feed vital pieces of equipment and machinery. Consider the internal combustion engine, for example. Impurities such as dirt and metal particles can damage internal components and cause excessive wear and eventual breakdown.

To help prevent such wear, the oil is run continuously through a filter designed to trap and filter out the impurities. Other piping systems need the same type of protection that the internal combustion engine does, which is why most piping systems include filters, strainers, and traps. These filtering components may prevent damage to valves, fittings, the pipe, and to downstream equipment/machinery. Chemicals, various types of waste products, paint, and pressurized steam are good examples of potentially damaging fluids. Filters and strainers play an important role in piping systems, protecting both the piping system and the equipment that the piping system serves.

Scaling

Since sodium and calcium hypochlorite are widely used in water and wastewater treatment operations, problems common in piping systems feeding this chemical are of special concern. Maintaining the chlorine in solution (used primarily as a disinfectant), sodium hydroxide (caustic) is used to raise the pH of the hypochlorite; the excess caustic raises the shelf life. A high pH caustic solution raises the pH of the dilution water to over pH 9.0 after it is diluted. The calcium in the dilution water reacts with dissolved CO₂ and forms calcium carbonate. Experience has shown that 2-in. pipes have turned into 3/4-in. pipes due to scale buildup. The scale deposition is greatest in areas of turbulence such as pumps, valves, rotameters, backpressure devices, etc. If lime (calcium oxide) is added (for alkalinity), plant water used as dilution water will have higher calcium levels and generates more scale. While it is true that softened water will not generate scale, it is also true that it is expensive in large quantities. Many facilities use softened water on hypochlorite mist odor scrubbers only. Scaling also often occurs in solution rotameters, making flow readings impossible and freezing the flow indicator in place. Various valves can freeze up and pressure sustaining valves freeze and become plugged. Various small diffuser holes fill with scale. To slow the rate of scaling, many facilities purchase water from local suppliers to dilute hypochlorite for the return activated sludge (RAS) and miscellaneous uses. Some facilities have experimented with the system by not adding lime to it. When they did this, manganese dioxide (black deposits) developed on the rotameter's glass, making viewing the float impossible. In many instances, moving the point of hypochlorite addition to downstream of the rotameter seemed to solve the problem. If remedial steps are not taken, scaling from

hypochlorite solutions can cause problems. For example, scale buildup can reduce the inside diameter of pipe so much that the actual supply of hypochlorite solution required to properly disinfect water or wastewater was reduced. Because of the scale buildup, the treatment system itself will not function as designed and could result in a hazardous situation in which the reduced pipe size increases the pressure level to the point of catastrophic failure. Scaling, corrosion, or other clogging problems in certain piping systems, are far from an ideal situation [14] Reducing substances deposition in the pipe system will reduce the cost of major revisions of the installation.

5. Modeling tritium extraction

The model for tritium extraction from organic phase in water was presented in the technical report for 12.2 Activity.

The model equations implemented in COMSOL allowed an estimation of distribution coefficient K_d of 1.01, which will be used for specific water consumption estimation.

GENERAL RECOMMENDATIONS ON THE TYPE, DESIGNING OF SPECIFIC EQUIPMENT AND CONSTRUCTION MATERIALS

According to the previously presented results of experimentally work, the designing of the industrial devices should consider the three steps to be followed: first a preliminary separation of the oil from wastewater for large quantities of water elimination, second the washing demulsification-deshydratation) step and finally the drying step. Each step use specific equipments mainly focused on the liquid-liquid contacting procedure. If a first separation oil-water cad be performed inside the storage vessel (for designing recommendation see 4th section in this report) the second and third steps will use different equipments.

Liquid-liquid contacting equipments may be generally classified into two categories: stagewise and continuous (differential) contact [4]

STAGewise EQUIPMENT (MIXER-SETTLERS)

The main function of a stage is to allow the equilibrium to be reached between liquids, equilibrium followed by a mechanical separation of the contacted liquids. Since this function means mixing the liquids and settling the resulting dispersion the devices are usually called mixer-settlers. The operation may be carried out in batch fashion or with continuous flow. If batch, the same vessel serve for both mixing and settling. If continuous, then separate vessels are usually but not always used. Batch-operated devices may use the same vessel alternately for the separate functions.

RATES OF MASS TRANSFER

Evaluating the extraction efficiency could be made using the overall “volumetric” mass-transfer coefficients, $K_C a_{av}$ or $K_D a_{av}$, or the equivalent stage efficiency. The coefficients K_C and K_D are made up of the coefficients for the individual liquids, k_C and k_D :

$$\frac{1}{K_D} = \frac{1}{k_D} + \frac{1}{m'_{CD} \cdot k_C}; \frac{1}{K_C} = \frac{1}{k_C} + \frac{m'_{CD}}{k_D}$$

The evidence is that the coefficients in continuous phase k_C , discontinuous phase k_D and the interfacial area a_{av} depend differently upon operating variables. For design, it is necessary to have separate information on the quantities k_C , k_D , and a_{av} . The role of an additional surface resistance is emphasized by the studies of Kishinevski and Moehalova [Zh. Prikl. Khim., **33**, 2049 (1960)].

Information on the coefficients is relatively undeveloped. Mainly the coefficients are strongly influenced by rate of drop coalescence and breakup, presence of surface-active agents, “interfacial turbulence” (Marangoni effect), drop-size distribution, and so on. [4]

Overall Coefficients and Stage Efficiency

If the values of a_{av} , k_C , k_D (and therefore K_D) can be estimated, the stage efficiency can be calculated through [4]:

$$E_{MD} = 1 - \exp\left(-\frac{K_D \cdot a_{av} \cdot Z}{u_D}\right) = 1 - \exp\left[-\frac{K_D \cdot a_{av} \cdot \theta \cdot (u_C + u_D)}{V_D}\right]$$

where Z is the height of liquid in vessel or mixer; for towers, height of packed section, θ the time of contact between phases, and u_C and u_D the superficial velocity of continuous/discontinuous phase.

For extraction, the mixing usually takes place either in a vessel which also serves as the settler (these can be baffled or unbaffled), or a separate mixing compartment (usually baffled if there is a gas-liquid interface, and usually unbaffled if it is liquid filled). The most common impellers are the marine impeller or disc flatblade turbine.

In scale-up, there are three types of similarity to be considered:

1. Geometric similarity. (Two vessels are geometrically similar if the ratio of all corresponding dimensions is the same)

2. Kinematic similarity. (Two vessels are kinematically similar if they are first geometrically similar and have the same ratio of velocities in corresponding positions of the vessel)

3. Dynamic similarity. (Two vessels are dynamically similar if they are first kinematically similar and all force ratios are equal in corresponding positions of the vessel.) For most liquid-liquid extraction applications, the mixing section are usually scaled up on the principle of geometric similarity and the power is based on maintaining the same power per unit volume. Treybal [9] demonstrates that, for geometrically similar vessels with equal holding time and power per unit volume, the stage efficiency for liquid extraction is likely to increase on scale-up, so this is generally a conservative approach.

Because of the difficulty in obtaining good data on mass-transfer coefficients and interfacial area as outlined earlier, it is necessary that bench or pilot scale experiments be performed to obtain the data needed for scale-up. The usual procedure is to determine a suitable range of residence times at various power inputs for a given mixer geometry. Most extractions are mass-transfer limited, so relatively short residence times

are adequate (in the range of 1–3 minutes). However in some cases (such as metal extractions), there is actually a reactive-extraction taking place, and residence time becomes more critical; times in the range of 10–15 minutes are not unusual. Besides looking at just the mixing, it is important at this time to also consider the settling time of the phases after mixing since this will impact on the settler design. Higher intensity of mixing may decrease the residence time for mass transfer, but at the same time create fine dispersions which are difficult to settle.

With the batch data, Slater and Godfrey in [15] recommend that an approach to equilibrium be used to provide the fundamental basis for scale-up; they define the approach to equilibrium (E_f) as:

$$E = \frac{C_i - C_t}{C_i - C_e}$$

It has been found that this data can be correlated for batch extraction using the following correlation:

$$1 - E_b = e^{(-k \cdot t_b)}$$

Once the value of k is obtained from the batch data, it can be related to a continuous extraction via the correlation:

$$E_f = \frac{k \cdot t_c}{1 + k \cdot t_c}$$

where E = approach to equilibrium of a single-stage contact

C_i = initial concentration

C_t = concentration at time t

C_e = concentration at equilibrium

E_b = approach to equilibrium for a batch process

E_f = approach to equilibrium for a continuous process

t_b = mixing time for a batch process

t_c = residence time for a continuous process

SETTLERS

Emulsions and Dispersions

The mixture of liquids leaving a mixer is a cloudy dispersion which must be settled, coalesced, and separated into its liquid phases in order to be withdrawn as separate liquids from a stage. For a dispersion to “break” into separate phases, both sedimentation

and coalescence of the drops of the dispersed phase must occur. Unstable dispersions usually have droplet diameters of about 1 mm or larger and settle rapidly. Stable dispersions, or emulsions, are generally characterized by droplet diameters of about 1 μm or less.

The “breaking” of a dispersion in a batch settler may be divided into two periods: (1) primary break, or rapid settling and coalescence of most of the dispersed phase, which often leaves a fog of very small droplets suspended as parts per million in the majority phase; and (2) secondary break, which represents the slow settling of the fog. Most industrial settlers are designed for the primary break since the slow secondary break would require much longer residence times. The small amount of entrainment to a subsequent stage seldom influences stage efficiency in a multistage cascade. However, for conserving solvent and desolventizing the effluent streams from the final stages of a cascade, it may be necessary to clarify as completely as possible, including the use of coalescers to eliminate secondary fog.

Sedimentation

Isolated droplets, settling or rising in a stagnant liquid under the force of gravity, generally move more rapidly than solid spheres. The rate of settling or rising is more rapid for large droplet size, large density difference between phases, and low viscosity of the continuous phase.

Coalescence The coalescence of droplets can occur whenever two or more droplets collide and remain in contact long enough for the continuous-phase film to become so thin that a hole develops and allows the liquid to become one body. A clean system with a high interfacial tension will generally coalesce quite rapidly. Particulates and polymeric films tend to accumulate at droplet surfaces and reduce the rate of coalescence. This can lead to the buildup of a “rag” layer at the liquid-liquid interface in an extractor. Rapid drop breakup and rapid coalescence can significantly enhance the rate of mass transfer between phases.

Gravity Settlers; Decanters (the most used in practice, recommended in this case)

These are tanks in which liquid-liquid dispersion is continuously settled and coalesced and from which the settled liquids are continuously withdrawn. They can be either horizontal or vertical.

MIXER-SETTLER COMBINATIONS

Any mixer and settler can be combined to produce a stage, and the stages in turn arranged in a multistage cascade. A great many commonly used arrangements have been developed in an effort to reduce or eliminate interstage pumping and to reduce costs generally. A compact alternating arrangement of mixers and settlers has been adopted in many of the “box-type” extractors developed originally for processing radioactive solutions, but now used in principle for many processes, with literally dozens of modifications. An example is the Pump-Mix mixer-settler in which adjacent stages have common walls [16]. The impellers in this case pump as well as mix by drawing the heavy liquid upward through the hollow impeller shaft and discharging it at a higher level through the hollow impeller. These extractors or variants of them have been built not only in relatively large sizes but also in miniature for bench-scale work.

CONTINUOUS (DIFFERENTIAL) CONTACT EQUIPMENT

Equipment in this category is usually arranged for multistage countercurrent contact of the insoluble liquids, without repeated complete separation of the liquids from each other between stages or their equivalent. Instead, the liquids remain in continuous contact throughout their passage through the equipment.

General Characteristics

Countercurrent flow is maintained by virtue of the difference in densities of the liquids and either the force of gravity (vertical towers) or centrifugal force (centrifugal extractors). One of the liquids is pumped through the equipment at any desired velocity. For the second the maximum velocity is then fixed; if it is attempted to exceed this limit, the second liquid will be rejected and the extractor will be flooded. The number of quantities that influence the rate of extraction is very large, and many of them are not well understood [4].

Axial Dispersion

The devices in this category are subject to axial (longitudinal) dispersion within both liquids and departure from strictly “plug,” countercurrent flow. The result of this axial mixing is to decrease the effective concentration driving force in the contactor so the towers must be taller than simple application of the plug-flow numbers of transfer units would indicate.

Packed Towers

For a packed-tower liquid-liquid extractor the empty shell of a spray tower is filled with packing to reduce the vertical circulation of the continuous phase. The standard commercial packings used in vapor-liquid systems are also used in liquid-liquid systems. This includes Raschig and pall rings, Berl and Intalox saddles, and other random-dumped packings as well as the newer structured packings. The available free space for flow is reduced by the packing but also the packing significantly reduces the height required for mass transfer. However, Nemunaitis, Eckert, Foote, and Rollinson [17] reported little benefit from a packed height greater than 3.05 m and recommended redistributing the dispersed phase about every 1.52 to 3.05 m to generate new droplets and mass-transfer surfaces. From this perspective the packing allows a wider spacing between sieve plates than described for a conventional sieve-plate tower. The pieces of random-dumped packing should be no larger than one-eighth of the tower diameter to minimize the wall effect which gives larger voids at the wall. The support for the packing can be an open

grid or multiarch support if the dispersed phase is distributed to the top of the bed. The packing support may also be a sieve plate with multiple light-liquid risers if the heavy phase is to be redispersed onto a lower bed. Or the packing support may be a sieve plate with multiple heavy-phase downcomers if the light phase is to be dispersed up into the bed. The streams of dispersed phase should be far enough apart to avoid coalescence at the dispersion plate, and the dispersed phase should not preferentially wet the packing. If the droplets wet the packing, they will coalesce and stream along the packing as rivulets. Perry's Chemical Engineers' Handbook [4] recommends the use of packed towers when the interfacial tension is below 10 mN/m (dyn/cm).

The holdup, flooding, mass transfer and the axial dispersion should be strongly studied inside the designing step.

Perforated-Plate (Sieve-Plate) Towers could be a good alternative to packed towers devices and economic criteria make the difference.

COUNTERCURRENT THEORETICAL STAGES

The liquid-liquid extraction process design imply to calculate the number of theoretical stages (or mass-transfer units) The main objective in this case is to evaluate the compromise between the size of the equipment, or number of contactors required, and the ratio of extraction solvent to feed flow rates required to achieve the desired transfer of mass from one phase to the other. In any mass-transfer process there can be an infinite number of combinations of flow rates, number of stages, and degrees of solute transfer. The optimum is governed by economic considerations. The operating cost of an extractor is generally quite low in comparison with the operating cost of the solvent recovery distillation column. The other common objective for calculating the number of countercurrent theoretical stages (or mass-transfer units) is to evaluate the performance of liquid-liquid extraction test equipment in a pilot plant or to evaluate production equipment in an industrial plant. Most liquid- liquid extraction equipment in common use can be designed to achieve the equivalent of 1 to 8 theoretical countercurrent stages, with some designed to achieve 10 to 12 stages [4].

Specific consumption of water

Establishing the specific consumption of water to reach a specified raffinate composition imply the crosscurrent theoretical stages number computing. After a single-stage liquid-liquid contact the phase remaining from the feed solution (raffinate) can be contacted with another quantity of fresh extraction solvent. The number of crosscurrent stages N that are required to reach a specified raffinate composition, in Bancroft coordinates, can be calculated directly if K_d is the partition coefficient, q_s the ratio of extraction solvent to feed solvent, X_B the required raffinate concentration and Y_B the extraction solvent concentration (considered fresh in each stage). As it was mentioned the solute concentrations are then given as the weight ratio of solute to feed solvent X and the weight ratio of solute to extraction solvent Y , i.e., Bancroft coordinates.

$$N = \frac{\lg \frac{X_{B,N} - Y_{B,0}/K_d}{X_{B,0}}}{\lg \frac{1}{1 + q_s \cdot K_d}}$$

where N is the number of contacts needed to reduce the tritium concentration in organic phase from X_{B0} to X_{BN} . The initial concentration of tritium in water Y_{B0} is zero.

Replacing in the above relation the experimental data linked to tritium concentration in organic and water, considering $q_s = 1$ and $K_d = 1.01$ (as it was found from experiments) results an $N = 0.6$ (so one contact is needed to diminish the concentration in organic from a concentration of 10^7 Bq/kg magnitude to 10^5 Bq/kg). It means (assuming that in each stage that the equilibrium is reached) a 1:1 ratio of organic/fresh water in the washing step. It should be mentioned that the crosscurrent scheme is not generally economically attractive for large commercial processes because solvent usage is high and solute concentration in the combined extract is low.

6 Experimental works performed at INRNE

Bulgarian partner-PP13 has conducted laboratory experimental works for removal radionuclides Sr, Fe, Ni and Pu from simulated secondary waste from the decontamination processes, applied at **the** Kozloduy NPP.

- **Determination of the capacity of Purolite-NRW 1600 with respect to ^{60}Co , ^{137}Cs and ^{241}Am , from a matrix of 0,5% HNO_3 , in the standby saturation of the resin.**



Figure 16. Capacity of Purolite-NRW 1600 with respect to ^{60}Co , ^{137}Cs and ^{241}Am

- **Determination of the selectivity of ion exchange resins Purolite NRW-1600 for radionuclides ^{137}Cs , ^{241}Pu , ^{94}Nb and ^{63}Ni contained in model solutions.** Test solutions containing known amount of standard cocktails including the radionuclides ^{137}Cs , ^{241}Pu , ^{94}Nb and ^{63}Ni were prepared. The conclusions are the following:

- Experimental results and retention and decontamination factors obtained show the applicability of ion-exchange resins NRW-1600 to decontamination of ^{241}Pu under the selected experimental conditions.

- When comparing the results for the retention and decontamination factors for the α -emitter ^{241}Pu , it is clear that the possibility of effective retention decreased with increasing column volumes omitted.

- The results for the retention and decontamination factors for the β -emitter ^{94}Nb are similar to that for ^{241}Pu . The possibility of effective retention decreased with increasing column volumes omitted.

- The ion-exchange resins NRW-1600 and NRW-160 are suitable for decontamination of ^{63}Ni originating from decontaminant matrix based on nitric acid.

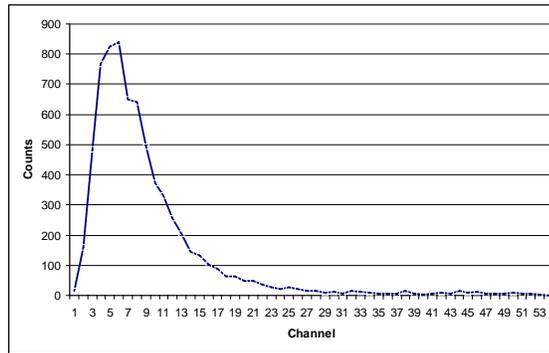


Figure 17. – spectrum of ^{241}Pu in a solution with matrix 0.5% HNO_3

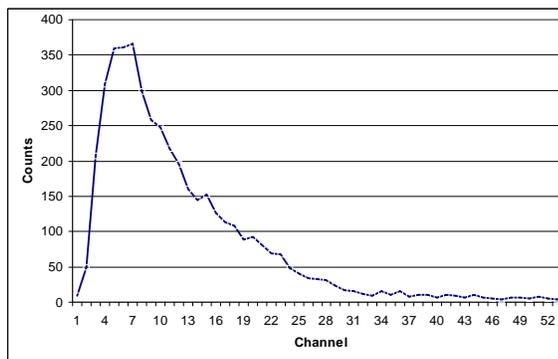


Figure 18. – spectrum of ^{241}Pu in a solution with matrix 10% $\text{H}_2\text{C}_2\text{O}_4$

- **Gamma spectrometry of ^{137}Cs :**

The resin NRW-1600 was preliminary conditioned with 5 column volumes of pure solution of 0.5% HNO_3 (used for decontamination of surfaces).

The test solution contained 0.5% HNO_3 to which a known quantity of radioactive ^{137}Cs was added. With the aim for obtaining measurable mass quantities also a stable isotope of Cesium was added as carrier. The model solution prepared this way was left for 10 days to achieve isotopic exchange and to become fully homogeneous. The homogenised solution was then let passing through the bed at a service flow rate of 10 BV/h (bed volumes per hour) at room temperature.

Figures 19 and 20 show the results obtained by gamma spectrometry of the initial solution and the eluate after the column.

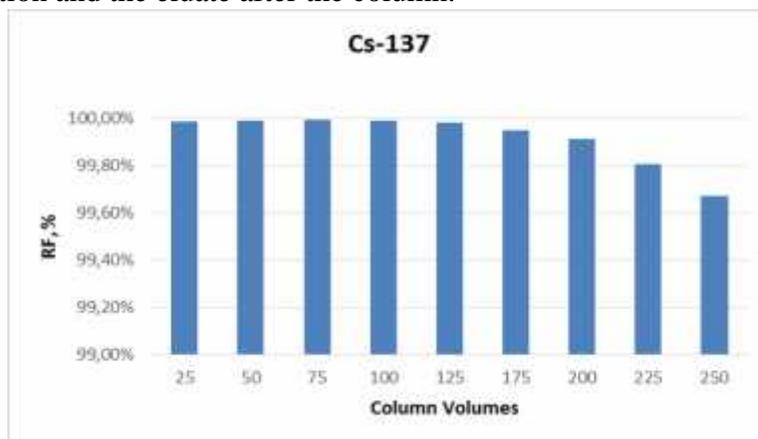


Figure 19. Retention factor of NRW-1600 with respect to ^{137}Cs in 0.5% HNO_3

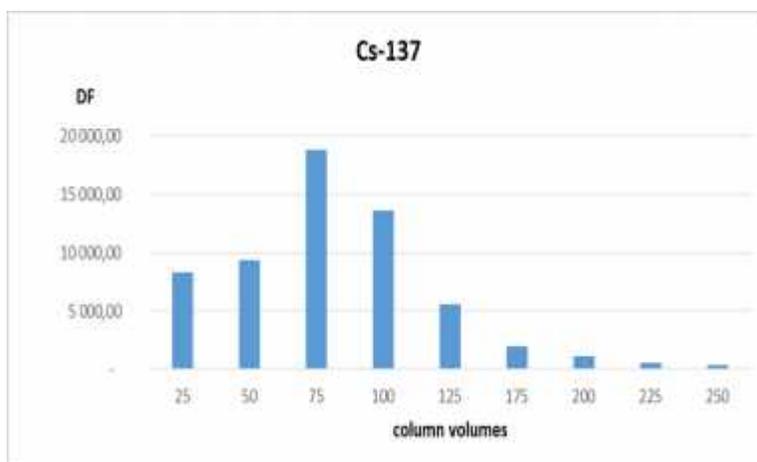


Figure 20. Decontamination factor of NRW-1600 with respect to ^{137}Cs in 0.5% HNO_3

- **Liquid-Scintillation Spectrometry of ^{241}Pu :**

The bed resin NRW-1600 was preliminary conditioned with 5 column volumes of pure solution of 0.5% HNO_3 .

The resin was tested with an initial solution containing 0.5% HNO_3 to which a known quantity of radioactive ^{241}Pu was added. The model solution prepared this way was left for 3 days to achieve isotopic exchange and to become fully homogeneous. The homogenized solution was then let through the bed at service flow rate of 10 BV/h (bed volumes per hour) at room temperature. For the ^{241}Pu activity determination, from the solution were taken by three aliquots of 10 ml each mixed with 10 ml scintillation cocktail ULTIMA GOLD™ LLT in the standard vessel for scintillation measurements. Analysis of aliquots of material before the bed and eluted solution was carried out by means of the Packard Instruments low-background Tri-Carb® 2770 TR/SL system (PACKARD TRI-CARB 2770 TR/SL) for liquid scintillation analysis. The experimental data were treated using the software package Quanta Smart and Microsoft Excel.

Figure 21 shows the results for the retention and decontamination factors for the ^{241}Pu -emitter.

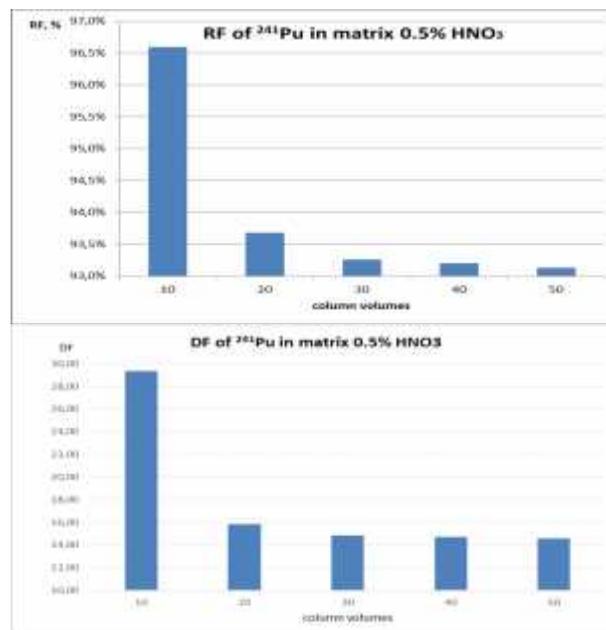


Figure 21. Retention and decontamination factors with respect to ^{241}Pu in 0.5% HNO_3

- Experimental results and retention and decontamination factors obtained show the applicability of ion-exchange resins NRW-1600 to decontamination of ^{241}Pu under the selected experimental conditions.

- When comparing the results for the retention and decontamination factors for the ^{241}Pu -emitter, it is clear that the possibility of effective retention decreased with increasing column volumes omitted.

- **Liquid-Scintillation Spectrometry of the ^{94}Nb -emitter**

The bed resin NRW-1600 was conditioned with 5 c.v. of pure solution of 0.5% HNO₃.

The test was carried out with an initial solution containing 0.5% HNO₃ to which a known quantity of radioactive ⁹⁴Nb was added. With the aim for obtaining measurable mass quantities also a stable isotope of Niobium was added as carrier. The experiment was performed by means of the pre-calibrated as specified above Packard Instruments low-background Tri-Carb® 2770 TR/SL system at room temperature using a model solution prepared in very similar way as for ²⁴¹Pu.

Figure 22 shows the results for the retention and decontamination factors for the -emitter ⁹⁴Nb

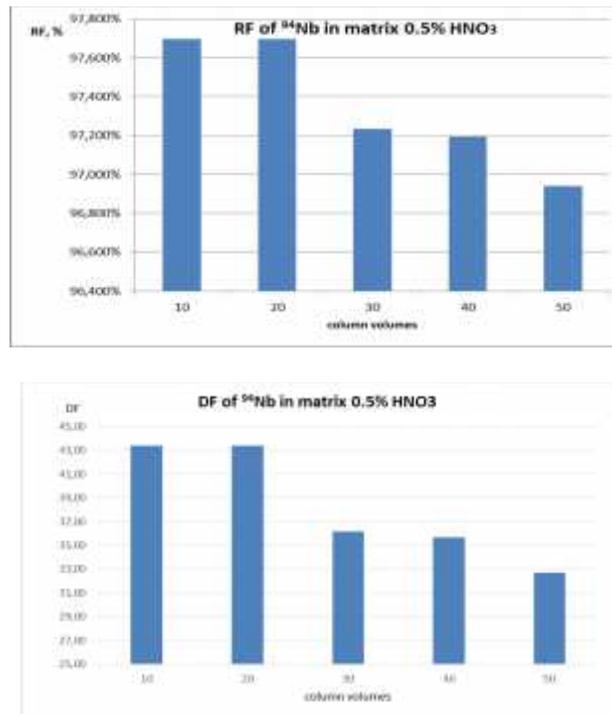


Figure 22. Retention and decontamination factors with respect to ⁹⁴Nb in 0.5% HNO₃

The results for the retention and decontamination factors for the -emitter ⁹⁴Nb are similar to that for ²⁴¹Pu. The possibility of effective retention decreased with increasing column volumes omitted.

- **Comparative measurements on the decontamination capacity of ion-exchange resins Purolite NRW-1600 and Purolite NRW-160 for the beta-emitter ⁶³Ni in a matrix of 0.5% HNO₃**

Experiments were conducted to compare the capacity of above said resins for ⁶³Ni. To a known volume of 0.5% nitric acid solution were added known quantities of the radioactive isotope ⁶³Ni and stable isotope of nickel as the carrier. The solution was

allowed to mature in order to achieve isotope exchange and complete homogenization. The solution was then passed through the said resins, conditioned preliminary with 5 column volumes of fresh solution of 0.5% nitric acid.

The samples were passed through the column at a speed of 25 column volumes per 1 hour. Fifty column volumes were passed through in 5 portions of 10 c. v. each one.

The decontamination factors for ^{63}Ni , under the particular conditions and matrix, were determined by liquid scintillation spectrometry using the spectrometer PACKARD TRI-CARB 2770 TR/SL.

For determining the activity of each solution of ^{63}Ni , by 3 aliquots of 2 ml each one were taken, which were mixed with 18ml of scintillation cocktail ULTIMA GOLD XR in a plastic cuvette.

The laboratory tests show that NRW-1600 and NRW-160 have a high selectivity for ^{63}Ni . The decontamination factors for ^{63}Ni of the two resins are presented in Figure 23.

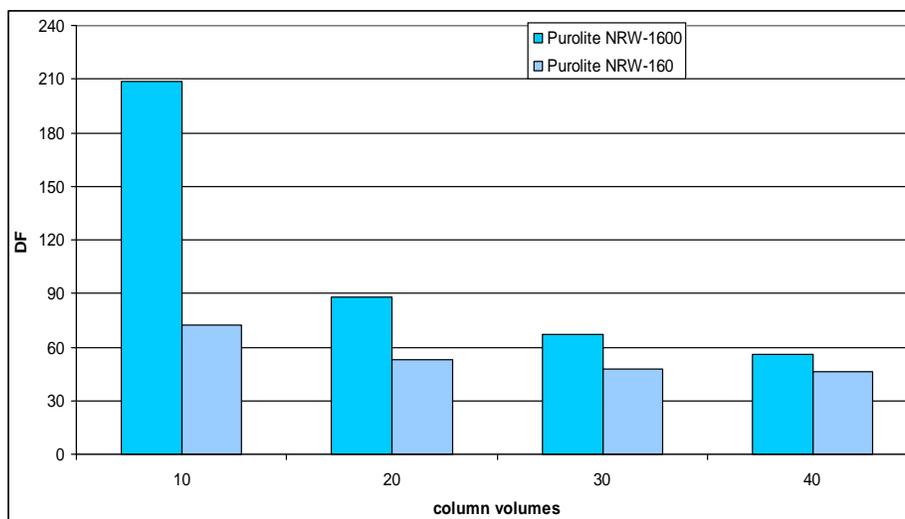


Figure 23. DF of Purolite NRW-1600 and Purolite NRW-160 for ^{63}Ni in 0.5% HNO_3 matrix

The results show that under the conditions of the experiment:

- The resin Purolite-NRW160 can be used for decontamination of the radionuclide ^{63}Ni , however the resin Purolite-NRW1600 is more effective for ^{63}Ni sorption of matrix solution with 0.5% HNO_3 .
- The capacity of both resins decreases with increasing volume of the passed through them model solution.

- **Gamma spectroscopic determination of the decontamination capacity of Purolite NRW-1600 for ^{241}Am , ^{137}Cs and ^{60}Co (Part 2.)**

First, the two gamma spectrometric systems with high purity Ge detectors of 50% and 20 % relative efficiency for the 1332 keV line of ^{60}Co were recalibrated with respect to energy and efficiency and comparative experiments for optimization of accuracy and counting time were carried out.

For the experiments test solutions were taken after transmission of the initial solution through columns loaded with preliminary conditioned resin volume of 2 ml: 200, 225 250 c. v. The samples after transmission through the columns were with a volume of 46.580 ml (for 200 c.v.); 50.070 ml (for 225 c.v.) and 49.840 ml (for 250 c.v.). The results from the gamma spectrometry measurements (Bq.l^{-1} , SE %) are displayed below.

Table 4. Results from the gamma spectrometry measurements (Bq.l^{-1} , SE %)

Sample	Sample type	^{241}Am , Bq.l^{-1} , (SE %)	^{137}Cs , Bq.l^{-1} , (SE %)	^{60}Co , Bq.l^{-1} , (SE %)
S - 0	Initial solution	216000 ± 11020 (5.1 %)	112600 ± 5193 (4.6 %)	57110 ± 2354 (4.1 %)
S - 1	25 column volumes	344.9 ± 27.6 (8.0 %)	< 5.82	73.21 ± 7.76 (10.6 %)
S - 2	50 column volumes	41.20 ± 4.29 (10.4 %)	10.25 ± 2.02 (19.7 %)	113.30 ± 5.55 (4.9 %)
S - 3	75 column volumes	33.61 ± 3.42 (10.2 %)	16.82 ± 1.93 (11.5 %)	174.40 ± 7.42 (4.1 %)
S - 4	100 column volumes	35.75 ± 4.50 (12.6 %)	28.47 ± 1.31 (4.6 %)	179.53 ± 7.18 (4.0 %)
S - 5	125 column volumes	37.36 ± 3.47 (9.3 %)	41.34 ± 2.86 (6.9 %)	184.4 ± 7.7 (4.2 %)
S - 6	150 column volumes	37.73 ± 4.60 (12.2 %)	42.81 ± 4.49 (10.5 %)	1243.0 ± 48.96 (3.9 %)
S - 7	175 column volumes	38.13 ± 3.24 (8.5 %)	43.14 ± 3.11 (7.2 %)	1359.0 ± 53.00 (3.9 %)
S - 8	200 column volumes	39.49 ± 3.39 (8.6 %)	251.70 ± 14.13 (5.6 %)	4000.00 ± 155.30 (3.9 %)

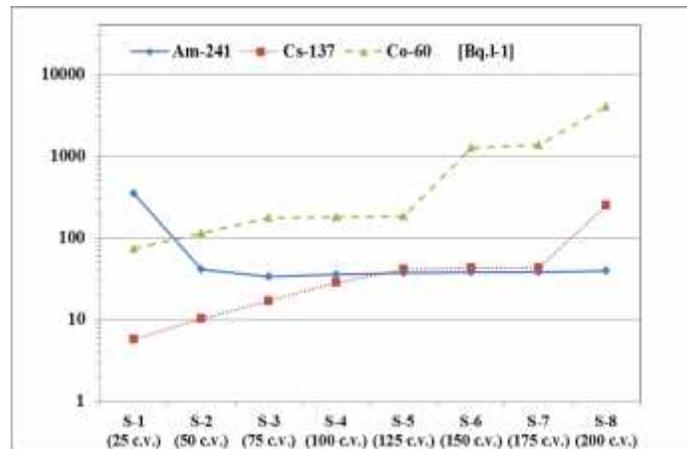


Figure 24. Variation of ^{241}Am , ^{137}Cs and ^{60}Co concentration after handling with the Purolite NRW-1600 resin.

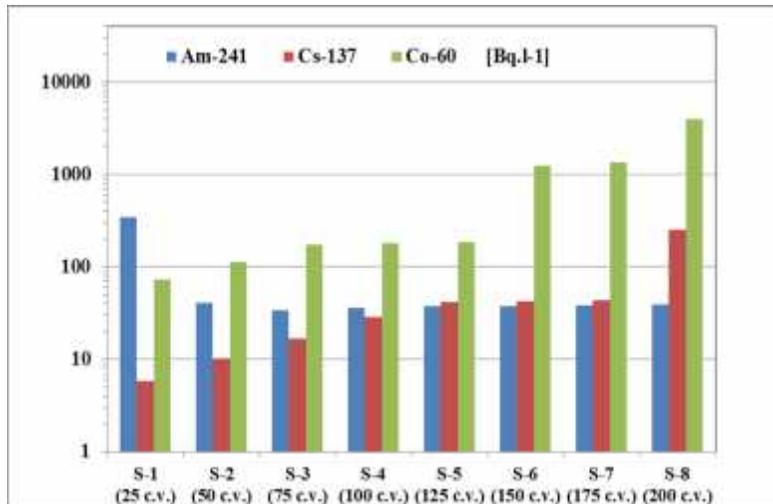


Figure 25. Histogram presentation of DF of Purolite NRW-1600 for ²⁴¹Am, ¹³⁷Cs and ⁶⁰Co

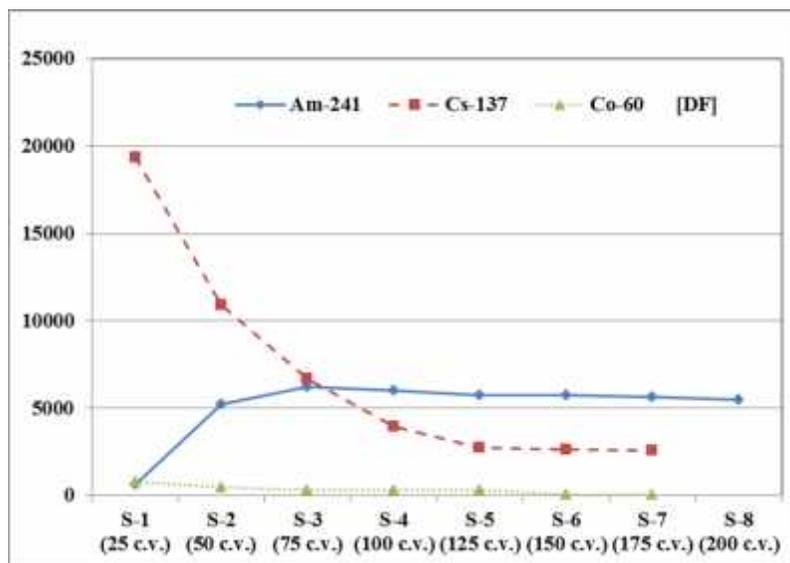


Figure 26. Decontamination factors (DF) of ion-exchange resin Purolite NRW-1600 for radionuclides ²⁴¹Am, ¹³⁷Cs and ⁶⁰Co.

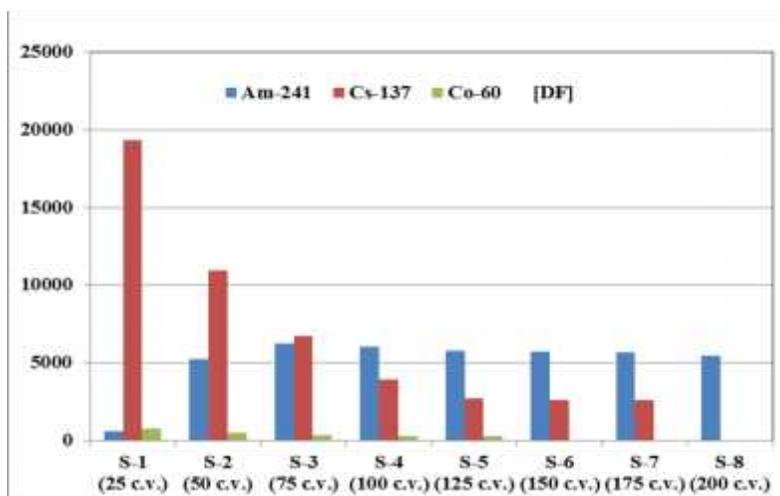


Figure 27. Histogram presentation of DF of Purolite NRW-1600 for ^{241}Am , ^{137}Cs and ^{60}Co

The obtained removed activity data show high percentage of retention of analyzed radionuclides (^{241}Am , ^{137}Cs , ^{60}Co). This result is confirmed also by the for the decontamination factors (DF) data. For decontamination of the radionuclide ^{63}Ni the resin Purolite-NRW160 can also be used, however the resin Purolite-NRW1600 is more effective for ^{63}Ni sorption of matrix solution with 0.5% HNO_3 .

Therefore, it can be concluded that under the conditions of present experiments the resin Purolite NRW-1600 is good cleaner for liquid radioactive wastes containing radionuclides such as ^{241}Am , ^{137}Cs , ^{60}Co and ^{63}Ni .

- **Determination of the amount of retained Co^{2+} in Purolite NRW 160 ion exchange resin**

Experiments were conducted to determine the degree of adsorption of Co^{2+} ions in the resin Purolite NRW 160 by measuring the time of mixing, in which the equilibrium is established. The amount of Co^{2+} ions retained in the volume of the resin is determined.

The preparation of the experiment included a theoretical study and preparation of the initial solution of known activity of ^{60}Co ;

Seven identical samples containing 100 mL of the first solution and 1 g of resin were prepared.

Description of the prepared samples:

- $1=100.03\text{g}$ (20,892 $\text{Bq}\cdot\text{g}^{-1}$)
- $2=100.03\text{g}$ (20,892 $\text{Bq}\cdot\text{g}^{-1}$)
- $3=100.03\text{g}$ (20,892 $\text{Bq}\cdot\text{g}^{-1}$)
- $4=100.02\text{g}$ (20,890 $\text{Bq}\cdot\text{g}^{-1}$)
- $5=100.04\text{g}$ (20,894 $\text{Bq}\cdot\text{g}^{-1}$)
- $6=100.00\text{g}$ (20,886 $\text{Bq}\cdot\text{g}^{-1}$)
- $7=100.00\text{g}$ (20,886 $\text{Bq}\cdot\text{g}^{-1}$)

Over different periods of time (5, 25, 45, 60, 70, 90 and 120 minutes) the samples were mixed and gamma spectrometric determination of the specific activity of ^{60}Co at the seven samples was performed. Before the measurements a recalibration of gamma spectrometric instrumentation and gamma spectrometric measurements on model samples was carried out. Treatment of the obtained spectra and analysis of results was performed. Discussion on the results was carried out with a view of optimizing the conditions of the experiments at next initial concentrations of solution.

Taking into account the conclusions from the above experiments the work continued with the next step as follows:

Starting solution of known ^{60}Co activity (20.13 Bq.g^{-1}) has been prepared from which 7 identical samples were made -each containing 100 mL from the initial solution and 1 g Purolite NRW 160. The samples were homogenized using an electromagnetic stirrer for different time periods: 5, 25, 45, 60, 70, 90 and 120 minutes. After that by an aliquot of 20 mL from the homogenized solutions were taken. These aliquot samples were diluted to a volume of 100 mL and the specific activity of ^{60}Co has been measured. The results are presented in Table 8.

Table 5. ^{60}Co specific activity (Bq.g^{-1}), DF and removed activity (%)

Sample	Co-60 removal time, [min]	Sample mass, [g]	Specific activity \pm Uncertainty, [Bq.g^{-1}]	Decontamination Factor (DF*),	Removed activity**, [%]
S-1	5	100.47	14.56 ± 0.39	1.38	27.54
S-2	25	100.52	12.02 ± 0.40	1.67	40.12
S-3	45	101.23	9.19 ± 0.33	2.19	54.34
S-4	60	100.24	5.40 ± 0.14	3.73	73.19
S-5	70	100.09	3.03 ± 0.08	6.64	84.94
S-6	90	100.45	2.98 ± 0.08	6.75	85.18
S-7	120	100.66	3.01 ± 0.08	6.69	85.05

* DF = Radiation level before decontamination/Radiation level after decontamination.

** % Activity removed = $(1 - (1/\text{DF}))100$

The gamma spectrometry measurements were carried out using HPGe detector (Ortec) with 54 % counting efficiency and energy resolution of 2.3 keV (at 1332 keV).

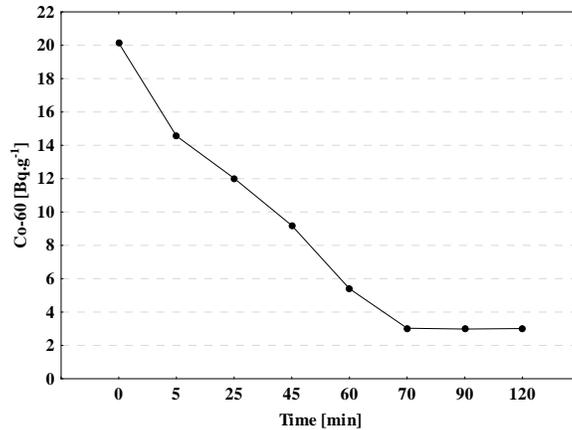


Figure 28. ⁶⁰Co specific activity in solution after interaction with the Purolite NRW 160 resin

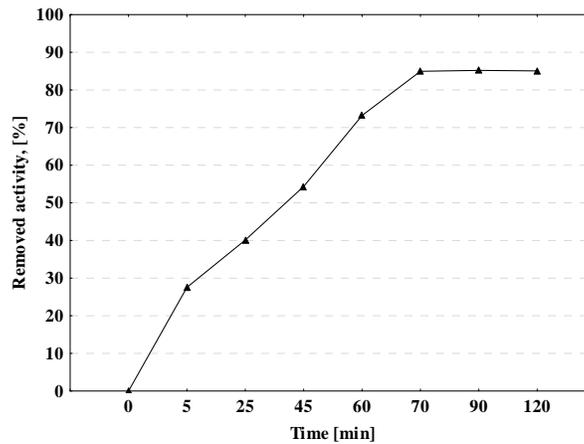


Figure 29. Effect of contact time on removal of ⁶⁰Co by Purolite NRW 160 resin

- **Determination of the amount of retained Co²⁺ in Purolite NRW 160 ion exchange resin by means of**

A spectrophotometric technique has been applied for determination of cobalt (Co) as Co²⁺. A Hach DR 2800 Portable Spectrophotometer has been used. For the experiment a starting solution with a concentration of 1,928 mg/ml of Co has been prepared.

The samples were pretreated with a cation exchange resin Purolite NRW 160, and the concentrations of Co²⁺ were measured at different period of times: 5, 25, 45, 60, 90 120 min.

For the spectrophotometric analyses to the samples were added additional reagents (EDTA, PAN, phthalate-phosphate).

After the sample is buffered and pyrophosphate is added to mask any Fe³⁺, the cobalt reacts with 1-(2-Pyridylazo)-2-Naphthol indicator (PAN) and the indicator forms complexes with most of the metals. After color development, EDTA is added to destroy

all metal-PAN complexes except cobalt. In the experiments the concentrations of 1,88 and 1,82 of Co are used. The results are shown in Fig.30.

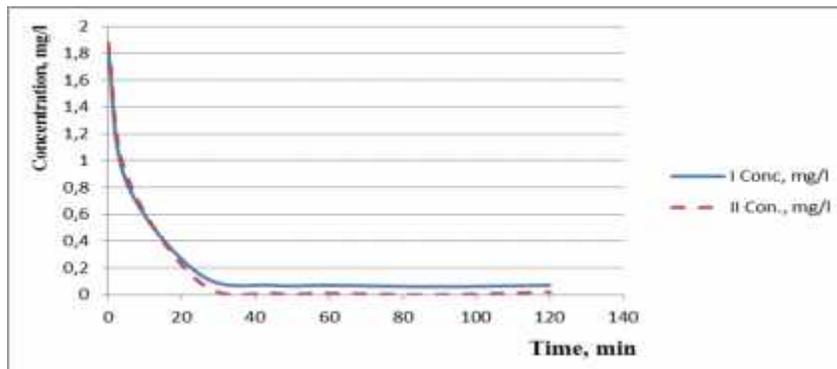


Figure 30. Time dependence for the initial concentration of 1,88 mg/L (I) and 1,82 mg/L (II) of Co after treatment with a cation exchange resin Purolite NRW 160

- **Simultaneous determination of the amount of retained Cobalt and Nickel by spectrophotometry (continuation)**

The 1-(2-Pyridiazo)-2-Naphtol (PAN) method has been successfully adapted and applied for determination of the amount of Co^{2+} and Ni^{2+} ions after treating test solutions with ion exchange resins. The method has been adapted on the basis of our previous experience in the analysis of presence of transition elements in water and wastewater. The Hach DR 2800 Portable Spectrophotometer has been used.

Short description: After pyrophosphate is added to buffer the sample and mask any Fe^{3+} , the nickel ions react with the 1-(2-Pyridylazo)-2-Naphthol indicator. The indicator forms complexes with most metals present. After color development, EDTA is added to destroy all metal-PAN complexes except nickel and cobalt. Spectrophotometers automatically adjust for cobalt interference by measuring the absorbance of the sample at both 560 nm and 620 nm. This method is unique because both nickel and cobalt can be determined on the same sample with a spectrophotometer. The results for nickel and cobalt are shown in Figure 31.

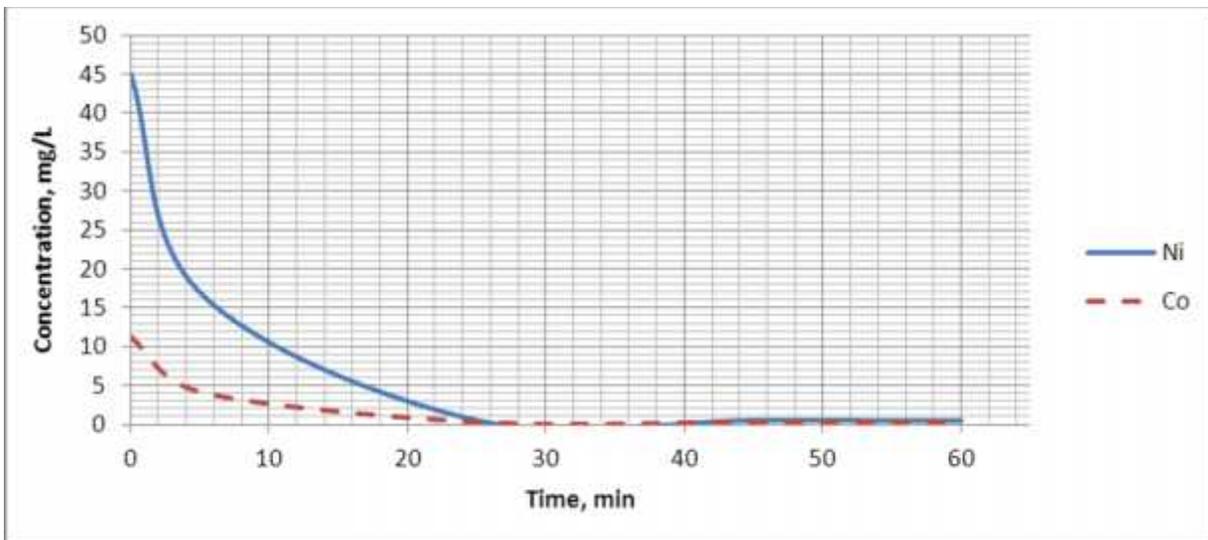


Figure 31. Most of the cobalt and nickel are absorbed from the resin on the 5-th minute.

The obtained removed activity data show high percentage of retention of analyzed radionuclides (^{241}Am , ^{137}Cs , ^{60}Co). This result is confirmed also by the for the decontamination factors (DF) data. For decontamination of the radionuclide ^{63}Ni the resin Purolite-NRW160 can also be used, however the resin Purolite-NRW1600 is more effective for ^{63}Ni sorption of matrix solution with 0.5% HNO_3 .

Therefore, it can be concluded that under the conditions of present experiments the resin Purolite NRW-1600 is good cleaner for liquid radioactive wastes containing radionuclides such as ^{241}Am , ^{137}Cs , ^{60}Co and ^{63}Ni .

In conclusion the resins Purolite NRW 160 and Purolite NRW 1600 are suitable for decontamination of radwaste water.

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