

RECYCLING URANIUM CONTAMINATED SCRAP WHICH CONTAINS IMPURITIES OF ALUMINIUM IN A FOUNDRY

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ABSTRACT

At their facilities in Krefeld, Germany, Siempelkamp Nuklear- und Umwelttechnik GmbH & Co (SNU) operates a plant for the recycling of metallic scrap with a low level radioactive contamination from nuclear industries. Since 1.1.1998 the recycling plant for scrap which is contaminated with naturally occurring radioactive materials (NORM) has been in operation. Both plants, each with a licensed capacity of 2.000 t/a, are operated with an adapted foundry-process. The radionuclides are concentrated in the slag, i.e. the melt is decontaminated and the produced ingots do not contain any detectable radioactivity.

When the scrap contains ^{60}Co or aluminium the free release of the ingots is not certain. Cobalt is soluble in the melt and the aluminium content in the melt correlates with the uranium in the melt. Additional treatment technologies are available for extracting the aluminium with the uranium as an accompanying element.

Based on this knowledge, the melting technology can be applied to an increased of input-materials to be recycled.

INTRODUCTION

640 offshore plants in the North Sea and the north-eastern regions of the Atlantic Ocean and many European gas and oil wells coproduce a significant amount of radionuclides, which contaminate the product-leading equipment. After their use, scrap with this contamination is unsuitable for direct recycling or reuse. (1, 2) According to the North Sea Conference in Portugal 1998, platforms may no longer be sunk within its area of jurisdiction. Decommissioning projects for this type of equipment will have to include two steps: Dismantling offshore and disposal or reuse onshore. This procedure requires special attention to contaminated components, i.e. NORM and mercury-contamination. The naturally occurring radionuclides in the scale being to the natural decay chains of ^{232}Th and ^{238}U . (3) Similar contamination is found on the scrap from other German gas-wells. (4, 5)

TREATING FACILITIES

At the CARLA - plant, SNU recycles low level radioactive scrap, coming from the nuclear industries. More than 12.000 Mg of metal-scrap with a specific activity below 200 Bq/g (Table I) is processed there already. (6) Since the issue of NORM contaminated scrap got more in public attention, recycling technologies for this kind of waste are recommended. As the CARLA plant is not equipped to treat mercury-contaminated materials, SNU modified the melting technology and put into operation the GERTA plant in Jan. 1998. Since then, 1.500 Mg of scrap has been molten, including 660 Mg of NORM-contaminated scrap with an activity < 500 Bq/g.

DECONTAMINATION PROCESS

Despite the different input criteria, licences and release limits for both plants, (Table I) the decontamination mechanism is similar in both facilities.

Table I: Licence framework

	CARLA	GERTA
Acceptance Criteria	NORM: < 1,000 Bq/g nuclear fuel: < 100 Bq/g and < 15 g/100 kg C^{14} , H^3 , Fe^{55} , Ni^{63} < 2,000 Bq/g Others: < 200 Bq/g	A_{tot} < 500 Bq/g Hg < 1 wt.-% organics < 5 wt.-%
Origin	Artificial radioactivity + NORM	Naturally occurring radioactivity
Release for melt	< 0.1 Bq/g < 1.0 Bq/g	no detectable activity
Release for slag	< 10^{-4} of the free release level according to German Radiation Protection Ordinance	A_{226Ra} < 65 Bq/g and A_{tot} < 500 Bq/g
Release for dust		
Authorisation	§3 German Radiation Protection Ordinance, based on Atomic Law	German law for the Protection of Air

Before starting the decontamination-process, the input-materials have to be dismantled to fit into the 3 Mg- (CARLA) or 8 Mg- (GERTA) induction-furnace. Then the material is fed into the furnace with the exhaust-system connected airtight with the furnace.

Using GERTA, organic impurities burn and mercury or lead vaporise. Mercury and lead are removed from the off gas in fabric filters and a fixed bed adsorber filled with activated carbon.

The CARLA-system provides a HEPA filter to remove the dust almost completely.

Melting the scrap, the elements uranium, thorium and radium and their radionuclides normally move into the slag because of their insolubility in the iron-melt. Slag forming additives improve this process. The slag swims on the surface of the melt and is taken off easily by a slag-grabber. The ^{210}Pb impurities in the input vaporise and are removed in the filter-systems. The decontamination of the melt is almost complete. (Table II)

Table II: Activity distribution after melting (8)

Nuclide	Melt	Slag	Dust
^{238}U , ^{235}U	1%	98%	1%
^{232}Th , ^{234}Th	< 1%	> 98%	1%
^{226}Ra , ^{228}Ra	-	98 %	2%
^{210}Pb	-	7 %	93%

The melt is poured from the furnace into the mould, forming the ingot, the main product of the process. Melting NORM scrap, these ingots are releasable and the slag as by-product as well.

Thus high percentage of the input-material comes out to be releasable. (Table III) Only the dust has to be disposed in an underground dump due to its mercury content.

Table III: Weight assessment

	Melt	Slag	Dust	Melting loss
Example 1 (7)	91%	5 %	1%	2 %
Example 2 (7)	87 %	11%	1,5 %	0,5 %
Example 3 (3)	88 %	11%	1%	-

PROBLEMS WITH DECONTAMINATION

Though most of the waste has been treated successfully some ingots are not releasable because they exceed the limits for free release. One reason is the solubility of radionuclides such as ^{60}Co , ^{55}Fe , ^{54}Mn and ^{63}Ni in the melt when scrap from nuclear industry is molten in CARLA.

There are also some ingots where the extraction of uranium and thorium did not succeed for reasons, unknown so far. This phenomenon is main focus of the following examinations:

EXPERIMENTS AND RESULTS

A program is carried out at SNU to solve the problem of the remaining uranium in some ingots.

1. Revealing the influence of different process parameters and the scrap-composition' on the decontamination.
2. Adapting the process in order to improve the decontamination of the melt.

Measurements and Analysis

To determine the activity in the melt, a gamma-spectrometric method is used. For this method, no chemical pre-processing is necessary before measurement. Only geometrical characteristics and density of the sample are important for determination of the activity. Therefore, a sample of the melt is poured into a standardised mould. Siempelkamp uses HPGe-detectors and an analysis software of EG&G Ortec. One of the detectors is equipped with a carbon window at the top. This allows the detector to measure gamma-energies down to about 5 to 6 keV, which is important for detecting the gamma-energy of ^{210}Pb at 46.5 keV with sufficient efficiency.

However, there may be more than one nuclide present in the sample within a specific gamma-energy-area. In this case, the analysis depends on the energy-resolution of the detector. If the activity determination is not clear, other nuclide energies must be evaluated. (8)

The measured activity serves as basis to calculate the concentration of the measured nuclides in the melt.

The concentration of the trace elements in the melt is detected with an atomic adsorption spectra analysis device. The 20 main elements are detectable by this method. (Table V)

Input Material

As input material for the experimental program we use different types of scrap contaminated by NORM and depleted uranium. (Table IV) Without the special treatment of the melt as described later in this paper, the produced ingots were not releasable, mainly due to their content of uranium nuclides.

Table IV: Input material

	GERTA	CARLA
	Exp. I	Exp. II and Exp. III
Contamination:	NORM	depleted uranium
Nuclides:	^{235}U ^{234}Th $^{234\text{m}}\text{Pa}$ ^{210}Pb ^{226}Ra ^{214}Pb ^{234}Bi	^{234}U ^{235}U ^{231}Th ^{234}Th ^{208}TI ^{212}Pb ^{212}Bi $^{234\text{m}}\text{Po}$ ^{238}U ^{228}Ac
Alloy	nickel	stainless-steel

In order to obtain comparable data, the scrap had to be treated at least once by the melting process. Then the melt has been in equilibrium with the slag. Further re-melting of these ingots under the same conditions would not produce a relevant amount of slag. An increase of the decontamination efficiency is impossible.

Correlation of Aluminium Content to Activity in the Treated Melt

The chemical analysis of the melt shows that all elements vary in common tolerance (Table V) To evaluate any deviation to the melt treated successfully, the elementary composition of a reference alloy is listed in this table. The investigation shows, that only the content of aluminium exceeds significant the reference values in all unreleased ingots. Problems with &contamination of aluminium scrap was already reported about. (9)

A closer view to the dependence of the content of aluminium and the remaining activity reveals a significant correlation. In order to verify this, more data are generated by extracting the aluminium from the melt into the slag by a method described later in this paper. All these data are at equilibrium between slag and melt. Additional data from former experiments are taken into consideration. 310 analyses of ingots produced between 1993 and 1998 at CARLA were evaluated and confirmed the first results (Example III).

In the range of 1 wt.-% to the detection limit of 0.001 wt.-% for aluminium an exponential correlation between the content of aluminium and the content of ^{235}U is found with a correlation-factor of $R^2 = 0.94$ over all samples. Taking into consideration only data from one melt during the extracting of aluminium at different points of equilibrium between slag and melt, this correlation factor reaches $R^2 = 0.99$ in Example II. (Fig. 1) Example I and II were molten in a furnace with basic refractory, using 75 % SiO_2 and 15% Al_2O_3 as flux.

Table V: Elementary analysis of the input

	GERTA	CARLA		
	Example I	Example II	Example III	References
	6 ingots	12 ingots	310 ingots	40 ingots
C	2.230 %	3.712 %	3.21 – 3.80 %	<3.680 %
Si	1.510 %	1.220 %	0.64 – 0.84 %	< 1.850 %
Mn	0.500 %	0.660 %	0.34 – 0.39 %	< 0.660 %
P	0.015 %	0.035 %	0.02 – 0.03 %	< 0.258 %
S	0.050 %	0.001 %		< 0.345 %
Cr	4.800 %	4.540 %	0.20 – 0.57 %	< 7.060 %
Mo	2.600 %	0.186 %	0.00 – 0.01 %	< 0.482 %
Ni	54.700 %	3.090 %	0.15 – 0.27 %	< 4.590 %
Al	0.260 %	0.444 %	0.12 – 0.60 %	< 0.072 %
Co		0.070 %		< 0.071 %
Cu	0.330 %	0.600 %	0.20 – 0.76 %	< 1.880 %
Nb	0.010 %	0.004 %	0.00 %	< 0.010 %
Ti		0.092 %	0.02 – 0.06 %	< 0.104 %
V		0.021 %	0.00 – 0.01 %	< 0.048 %
W		0.019 %		< 0.680 %
Pb	0.005 %	0.029 %	0.00 – 0.01 %	< 0.087 %
Sn	0.004 %	0.019 %	0.02 – 0.03 %	< 0.015 %
As		0.011 %		< 0.024 %
B		0.001 %	0.00 %	< 0.035 %

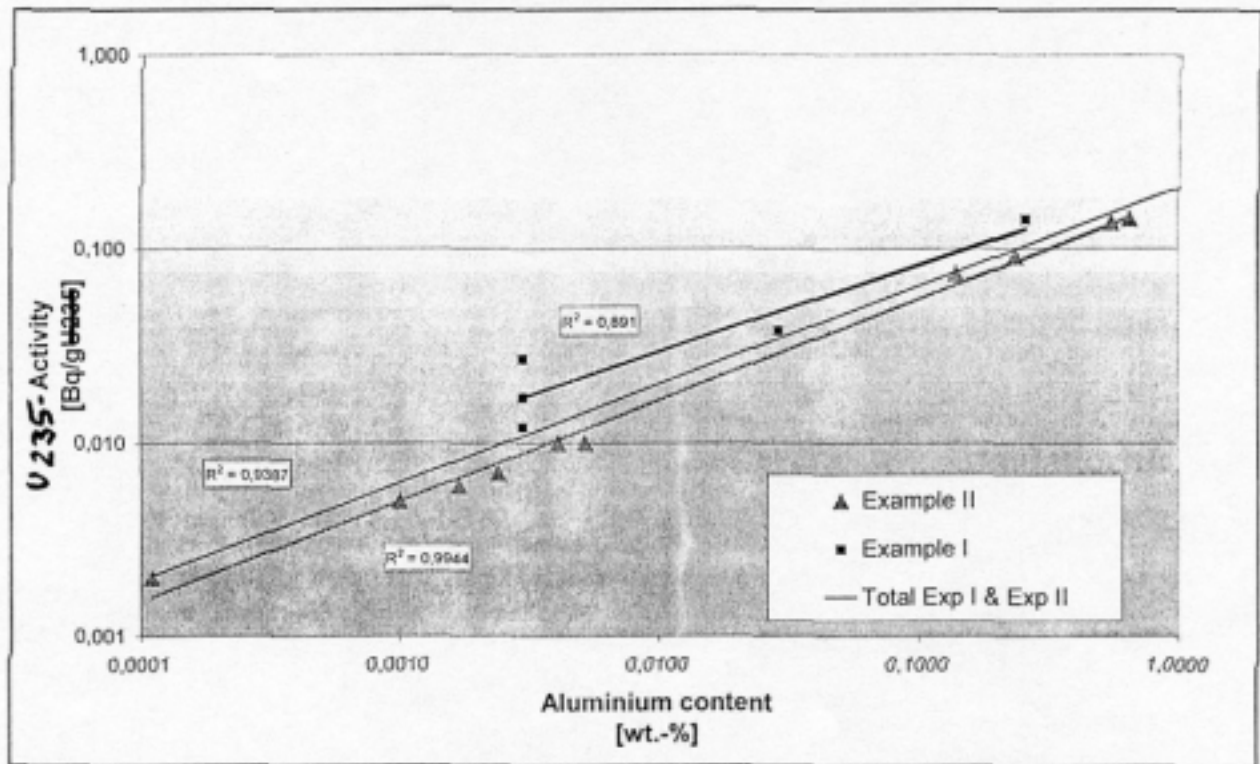
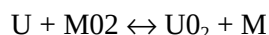


Fig. 1: Correlation between activity and aluminium content in the melt

Extracting Uranium from the Melt in Presence of Aluminium

The content of aluminium prohibits the transfer of uranium into the slag. The oxidation-reduction reaction of uraniumoxide (UO_2) with metal (M) occurs as

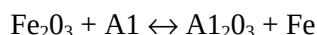


The reduced uranium and metal would form an intermetallic compound that is solved in the melt and cannot be transferred to the slag. in this case with iron as reactant M the equilibrium is on the side of UO_2 . (10)

However, extracting the aluminium from the melt seems to solve the problem.

Therefore three different additives are tested to reduce the aluminium content:

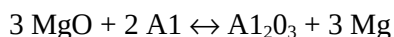
1. Fe_2O_3 (hematite): The hematite reacts with the aluminium in the melt as follows:



For the test, the hematite was added stoichiometric with aluminium to the melt.

2. After taking out the slag, in a second step the same amount of hematite was added again to improve the aluminium removal. The slag formed then is removed also.

2. In a third step, the melt was treated by MgO :



The added amount of MgO was twice the stoichiometric need of MgO according the reaction-equation. In order to improve the reaction, the MgO was put in the ladle first, before pouring the melt.

This procedure was tested with both examples with similar results. The content of aluminium was reduced in the melt significantly. The other elements measured by AAS were not affected by the treatment. (Fig. 2)

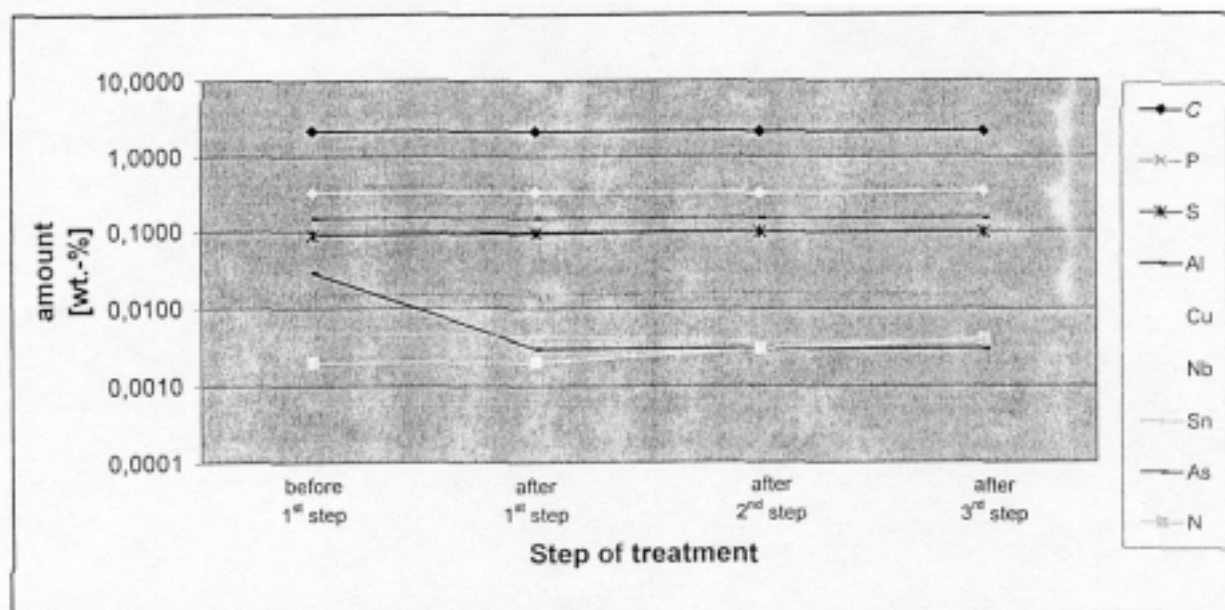


Fig. 2: Progress of extraction of aluminium

In this case, the stoichiometric addition of hematite leads to the lowest in the content of aluminium in the melt. By extracting the aluminium, uranium was also transferred to the slag. The remaining activity in the ingot was far below the limit for free re-use. (Fig. 3)

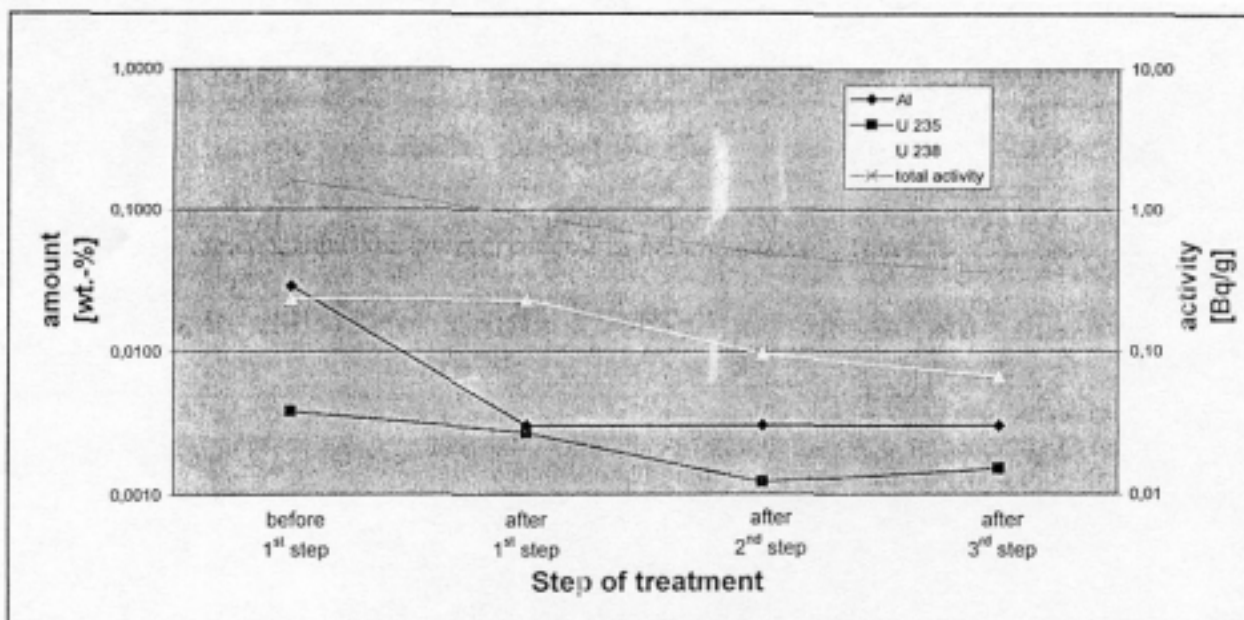


Fig. 3: Effect of the treatment on decontamination.

In the process of treating example II is shown. Due to the size of the ingots they did not fit in the furnace at once. Therefore, the melting process was started by melting the first half of the ingots (step 1). The remaining ingots were added later in step 4 into the molten iron.

Table VI: Procedure of treatment

1.	Melting of the first ingots (3.775 t)
2.	Slagging by using Al_2O_3
3.	Adding Fe_2O_3 Slagging by using Al_2O_3
4.	Adding Fe_2O_3 Slagging by using Al_2O_3
5.	Adding Fe_2O_3 Slagging by using Al_2O_3
6.	Adding Fe_2O_3 Slagging by using Al_2O_3
7.	Adding MgO Slagging by using Al_2O_3

In step 2, slag was removed from the surface by using Al_2O_3 and SiO_2 as slag forming additive. In step 3, hematite was added in a stoichiometric relation and the furnace run 30 min before the newly formed slag was taken out.

After having added the remaining ingots up to the total content of melt in the furnace (7.402 Mg), in step 5 hematite is added stoichiometrically and in step 6, twice this amount of Fe_2O_3 . Every step was followed by the removal of slag.

As the final step of treating, MgO was added and the slag removed again. The remaining activity in the melt reached $A_{235\text{U}} = 0.005 \text{ Bq/g}$. The produced ingots were releasable for free re-use. With an activity of $A_{235\text{U}} = 0,118 \text{ Bq/g}$ at the beginning of the treatment, a decontamination of 97 % was realised.

For both examples, the first addition of Fe_2O_3 to the melt was the most efficient under the aspect of aluminium removed, absolute and relative. (Fig. 2 and Fig. 4) The efficiency of uranium decontamination follows this function.

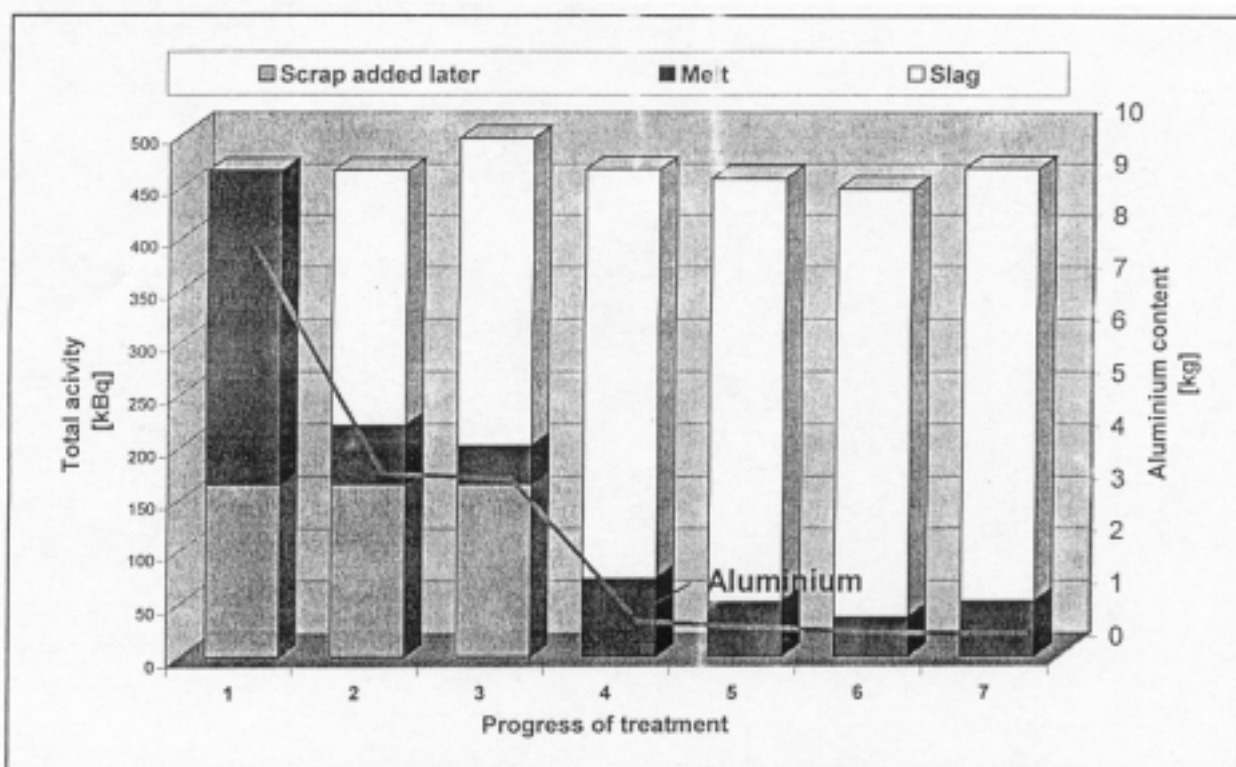


Fig. 4: Distribution of the activity and the aluminium during the treatment

CONCLUSION

The described investigation leads to two results:

The correlation between the aluminium-content in the melt and the decontamination of the melt by slagging is obvious. Even if the mechanism has to be explained in the further tests, the knowledge about the influence leads to an improvement of the uranium removal.

Two methods were tested in the described first step of investigation. Both methods lead to an oxidation of aluminium to transfer the aluminium-oxide into the slag. The oxygen was added by feeding hematite or magnetite to the melt. With both additives, the transfer of aluminium into the slag and the decontamination were successful.

Applying this method, the GERTA-/CARLA technology increases the range of input-materials which can be recycled to obtain a releasable product. These ingots meet the specifications for the steel-making industries.

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