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Characterization of naturally occurring radioactive materials and Cobalt-60 contaminated ferrous scraps from steel industries

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Abstract

Since the occurrence of radioactively contaminated rebar incident in 1992, steel industries in Taiwan were encouraged by Atomic Energy Council (AEC) to install portal monitor to detect the abnormal radiation in shipments of metal scrap feed. From 1994 through 1999, there were 53 discoveries of radioactivity in ferrous scraps by steel companies. These include 15 orphan radioactive sources, 16 cobalt-60 contaminated rebars, 20 Naturally Occurring Radioactive Material (NORM) contaminated scraps, and two unknowns. Most NORM-contaminated scraps were from abroad.

The NORM and cobalt-60 contaminated scraps were taken from the steel mills and analyzed in laboratory. The analytical results of scales and sludge sampled from NORM-contaminated scraps combining with the circumstantial evidences indicate that five possible industrial processes may be involved. They are oil production and treatment, heavy mineral sand benefication and rare earth processing, copper mining and processing, recovery of ammonium chloride by lime adsorption in Ammonium-soda process, and tailing of uranium enrichment process.

The cobalt-60 activity and trace elements concentrations of contaminated rebars confirm that all of them were produced domestically in the period from Oct. 1982 to Jan. 1983, when the cobalt-60 sources were lost and entered the electric arc furnace to produce the contaminated rebars.

1. INTRODUCTION

Since the occurrence of radioactively contaminated rebar incident in 1992, steel industries in Taiwan were encouraged by AEC to install portal monitor to detect the abnormal radiation in shipments of metal scrap feed [1]. From 1994, the radiation source devices, Co-60 contaminated rebars, and NORM-contaminated metals have been discovered in shipments of metal scrap, and the number of discoveries was generally increasing every year. Most NORM-contaminated scraps were from abroad, especially from U.S., South Africa, and Australia where plants of the process industry were dismantled [2].

The discovery of radioactive scrap presents a vexing problem to steel industry. The current industry practice is to store the contaminated scraps temporarily or to return scraps to the supplier. It is quite costly and manpower consumptive. Furthermore, melting radioactive scraps could threaten worker safety and health and is potentially harmful to consumers and environment [3-6]

Department of Radiation Protection, AEC initiated a project [2] to characterize the NORM and cobalt-60 contaminated scraps by radiochemical methods and to study the origin of its industrial process. The aim is to provide proper information and observation to competent authority to stop the import of contaminated scraps and protect general public from accidental radiation exposure.

2. EXPERIMENTS

For the study of industrial origin of NORM-contaminated scrap, about 50 grams of scale, sludge, and process material absorbed on the scraps (pipe, valve and tank wall) from steel mills were sampled and analyzed in laboratory. The activity concentrations of ^{226}Ra (or ^{238}U) and ^{228}Ra (or ^{232}Th) were measured from their progeny of ^{214}Bi (609.3 keV) and ^{228}Ac (911.1 keV) respectively by gamma spectrometer equipped with HPGe detector and multichannel analyzer under secular equilibrium condition. The morphology of sampled materials was characterized by scanning electron microscopy equipped with energy dispersion spectrometry (SEM-EDS) and X-ray diffraction (XRD) technique. In addition, $^{235}U/^{238}U$ ratio of depleted uranium was measured by inductively-coupled plasma mass spectrometry (ICP-MS).

To make a comparison among the ^{60}Co-contaminated rebars, about 0.5 gram of metallic scrap were sampled and dissolved in 1:1 nitric acid solution. The activity of ^{60}Co was measured at 1173 keV and 1332 keV by the above-mentioned gamma-ray spectrometer and corrected to the first sampling date (March 31, 1994) for the sake of comparison. The concentrations of trace elements (Cr, Cu, Mn, Ni and Si) in rebar were determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES).

3. RESULTS AND DISCUSSION

3.1. Radioactivity discovered from steel mills in Taiwan

Table I summarized the discoveries of radioactively contaminated scraps from steel mills in Taiwan since 1994 [2]. The radioactively contaminated scraps can be categorized as radiation sources, ^{60}Co-contaminated rebars, and NORM-contaminated scraps. It can be seen from Table I that a total of 53 discoveries were observed and number of discoveries was increasing every year. Except that the ^{60}Co-contaminated rebars were produced domestically, most radiation sources and NORM-contaminated scraps were from abroad, especially the NORM-contaminated scraps were from U.S., South Africa, and Australia where plants of the process industry were dismantled.

3.2. Industrial origin of NORM-contaminated scraps

Table II summarized the analytical results of NORM-contaminated scraps from steel mills only if the industrial origin could be identified. It can be seen that both scale and sludge with composition of divalent metallic sulfate have higher activity concentration of ^{226}Ra or ^{228}Ra. This reflects that Group IIA elements will coprecipitate easily to form complex inorganic sulfates.

Scale sample 951206 taken from 4" steel pipe was imported from Amsterdam, The Netherlands. It has an average 1.25 mm of thickness and contains 212.6 Bq/g and 100.4 Bq/g of ^{226}Ra and ^{228}Ra respectively with composition of $Ba_xSr_{1-x}SO_4$ (x=0.75). The SEM study shows that the scale consists of large and well-defined tabular mixed crystals (Fig. 1). Scale formation and growth on the pipe is quite analogous to the pipe scale in oil production facility [7, 8]. Meanwhile, a ^{226}Ra source was discovered in the same shipment, we therefore could reasonably speculate that this shipment of scraps was dismantled from oil production industry [9].

Samples 971212-1,2 taken from steel pipe and cover were imported from Australia. Scale 971212-1 consists of $Ba_xSr_{1-x}SO_4$ (x=~0.75) and contains 230.9 and 758.5 Bq/g of ^{226}Ra and ^{228}Ra respectively. Sludge 971212-2 consists of $Ce(Th)PO_4$, $FeTiO_3$ and $ZrSiO_4$ and contains 13.5 and 94. 4 Bq/g of ^{238}U and ^{232}Th respectively. SEM-EDS also shows that a single grain of sludge represent a type of mineral and the amounts of grains are in the order of zircon, ilmenite and monazite (Fig. 2). It is obvious that this shipment of scraps could be originated from a heavy mineral sand benefication and rare earth processing plant [10].

TABLE I. SUMMARY OF RADIOACTIVELY CONTAMINATED SCRAPS DISCOVERED BY STEEL MILLS (from June, 1994 to June, 1999) [2]

Category	Year						Total
	1994	1995	1996	1997	1998	1999	
Orphan radiation source	0	3	1	3	6	2	15
^{60}Co contaminated rebar	0	5	2	4	1	4	16
NORM contaminated scrap	1	1	1	3	11	3	20
Unknown	-	-	1	-	1	0	2
Total	1	9	5	10	19	9	53

TABLE II. ANALYTICAL RESULTS OF SAMPLES TAKEN FROM NORM-CONTAMINATED SCRAPS

Sample Number[1]	Country of Origin	Characterization	Chemical Composition	$^{226}Ra(^{238}U)$, Bq/g	$^{228}Ra(^{232}Th)$, Bq/g
951206	The Netherlands	Pipe scale, 0.5~3.7 μSv/h	$Ba_{0.75}Sr_{0.25}SO_4$	212.6±0.4	100.4±0.8
971212-1	Australia	Pipe scale, 64~75 μSv/h	$Ba_{0.75}Sr_{0.25}SO_4$	230.9±2.6	758.5±10.2
971212-2	Australia	Sludge, 1.2~2.4 μSv/h	$Ce(Th)PO_4$, $FeTiO_3$, $ZrSiO_4$	(13.5±0.4)	(94.4±1.4)
980105	South Africa	Pipe scale, 92 μSv/h	$PbSO_4$, $CuSO_4$	12,800±66.4	<LLD
981012-1	Yi-Lan, Taiwan	Pipe scale, 10 μSv/h	$(Mg,Ca,Sr,Ba)SO_4$	393±2.83	9.67±1.65
981012-2	Yi-Lan, Taiwan	Process material, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990111-1	Yi-Lan, Taiwan	Tank scale, ~2 μSv/h	$(Mg,Ca,Sr,Ba)SO_4$	379±1.1	4.53±0.62
990111-2	Yi-Lan,, Taiwan	Process material, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990202-1	Scrap yard, Yi-Lan	Sludge, ~2 μSv/h	-	21.7±0.11	<LLD
990202-2	Soda Mfg. Co. Ltd., Yi-Lan, Taiwan	Lime slurry, b.g.	$Ca(OH)_2$, $CaCO_3$	<LLD	<LLD
990517	Hong Kong	Metal block, ~45 μSv/h (25 cm L×10 cm W×8 cm H, 14.56 kg)	U(99.9%), $^{235}U/^{238}U$ (0.212%)	-	-

[1] According to the date of discovery.

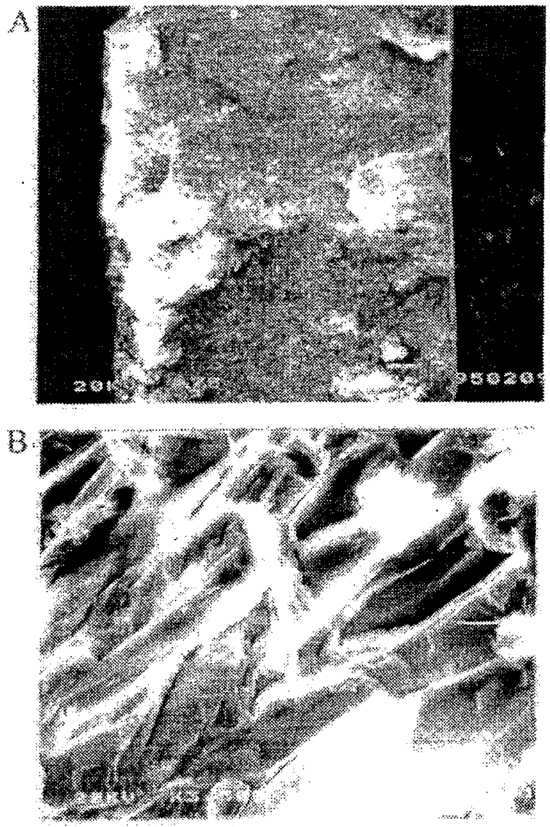

FIG.1. SEM photographs. A – Cross section of scale (75X), B – Close-up of internal scale (3500X).

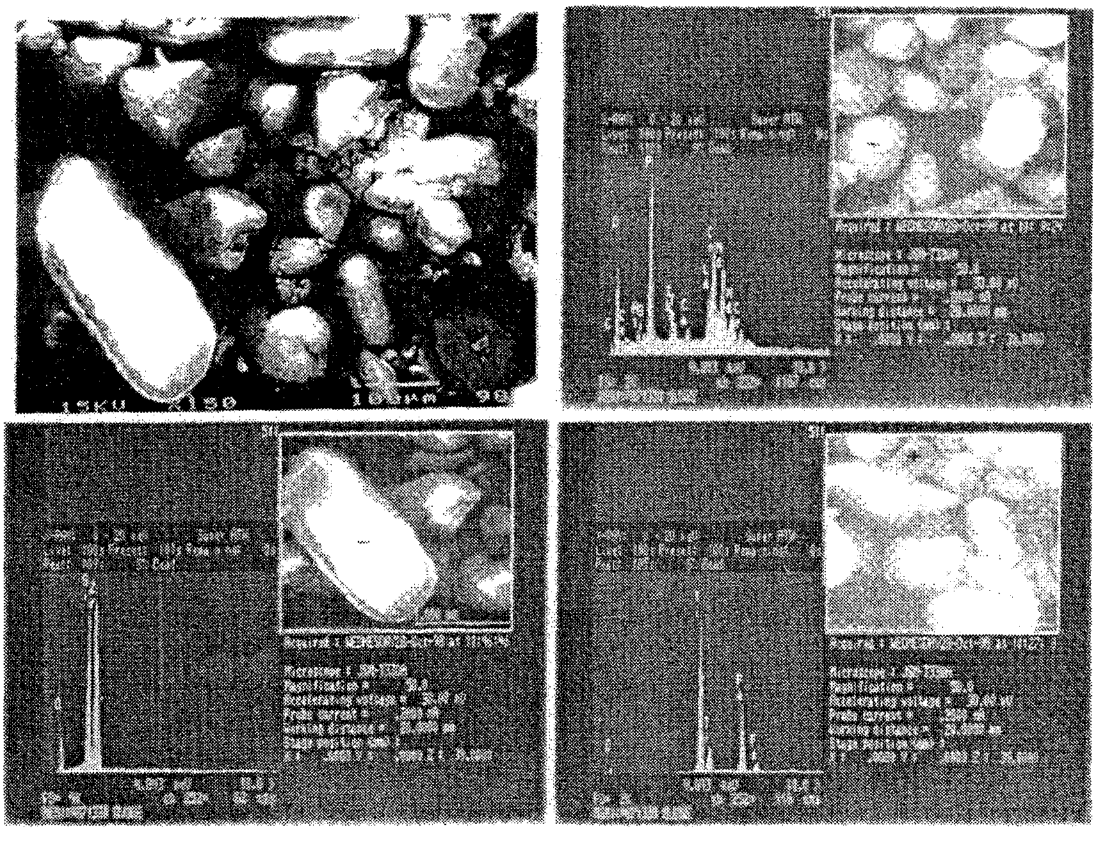

FIG. 2. Single grain analysis by SEM-EDS.

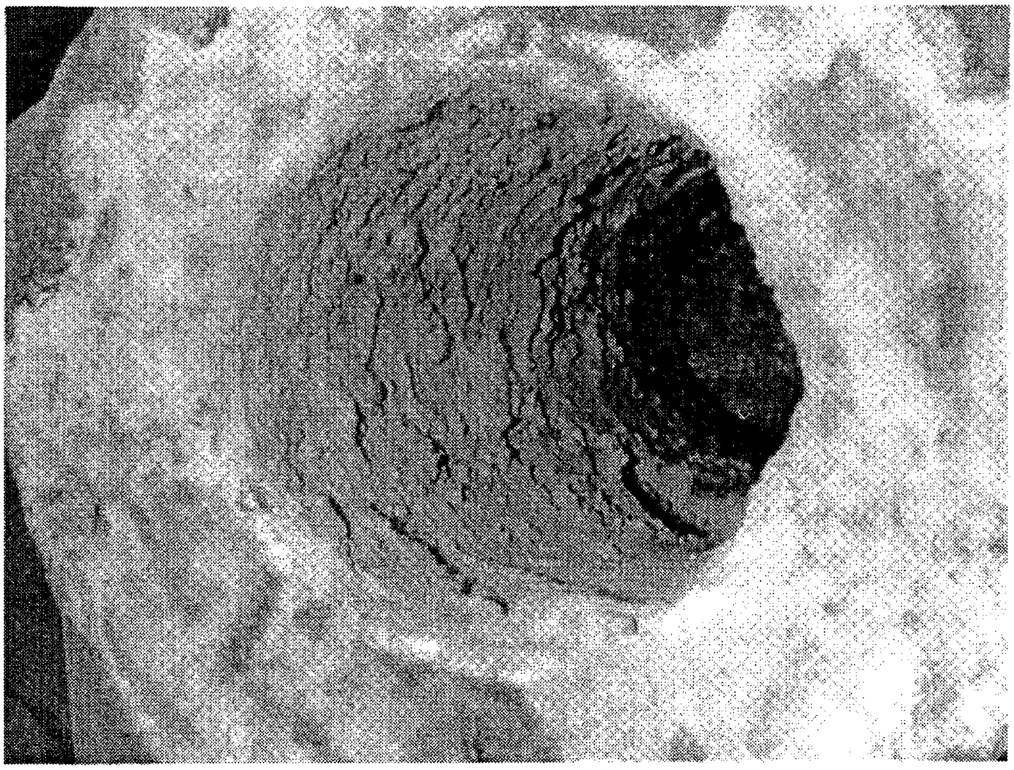

FIG. 3. Pipe scale and process materials.

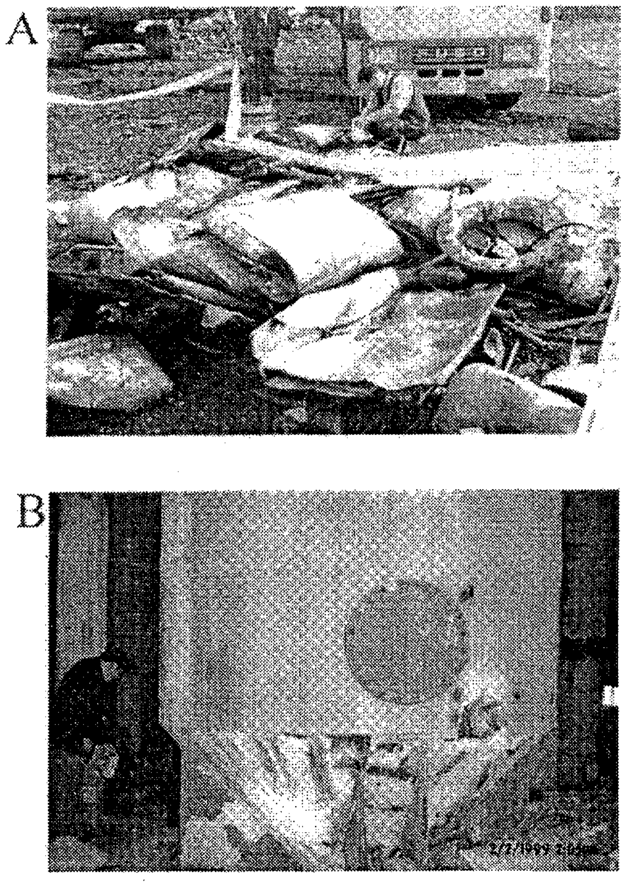

FIG. 4. NORM contaminated scraps. A – discovered by steel mills, B – Ammonium chloride adsorption tank left in Soda ash manufacturing company.

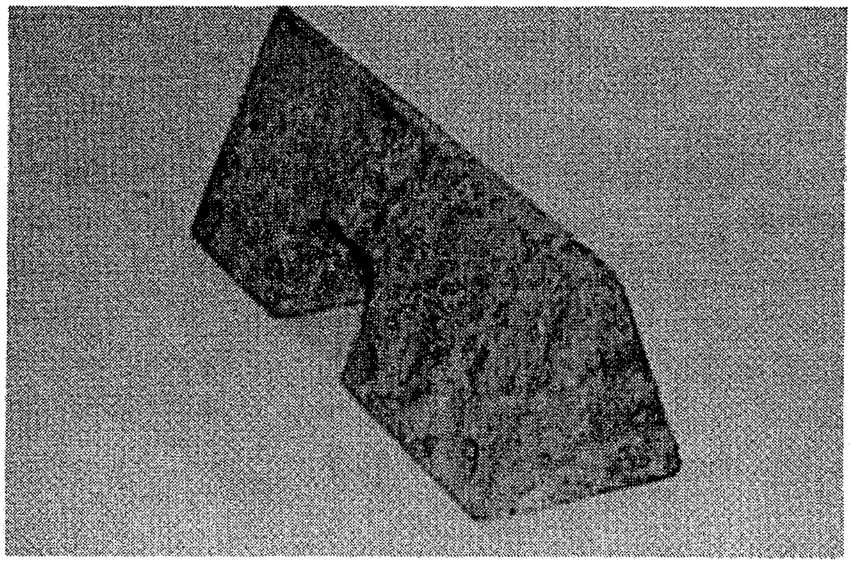

FIG. 5. Photograph of depleted uranium counterbalance weight (~45 μSv/h, 25 cm L×10 cm W×8 cm H, 14.56 kg).

Sample 980105 taken from steel pipe was imported from South Africa. It consists of $PbSO_4$ and $CuSO_4$ and contains 12,800 Bq/g of ^{226}Ra only. According to literature [11], the main ore mineral in Palabora, South Africa is chalcopyrite ($CuFeS_2$) and the uranium occurs in uranothorianite. In addition, pyrite, magnetite, quartz, calcite, sphalerite (ZnS), and galena (PbS) exit together. The copper is produced from an open pit mine and uranium is recovered as a by-product from mining at Palabora. The analytical results combining with the circumstantial evidences indicate that this shipment of scraps could be originated from copper mining and processing industry.

Three steel mills in northern Taiwan discovered abnormal radiation in their shipments of scrap provided from the same supplier in the period of October 1998 to January 1999. Sample 981012-1, 2 and 990111-1, 2 were the scales and process materials taken from the scraps of two steel mills, respectively (Fig. 3 and 4A). The analytical results show that both scales consist of (Mg, Ca, Sr, Ba)SO_4 and process materials consist of $Ca(OH)_2$ and $CaCO_3$, and only scales contain average of 386 Bq/g and 13.7 Bq/g of ^{226}Ra and ^{228}Ra respectively. The process materials indicated that the scraps could be dismantled from soda ash related industry. A soda ash manufacturing company near scrap yard at Yi-Lan, Taiwan was identified from sales record and confirmed by radiation survey. This company was established 40 years ago and produced $NaHCO_3$ and Na_2CO_3 by Ammonia-soda process. The reaction product, ammonium chloride, is then recovered by lime slurry adsorption. Although the detailed mechanism of radioactive scale formation is unknown, the old process was dismantled several months ago. One of the adsorption tank left there to store ammonium chloride and the other one still on production showed an abnormal radiation (~2 μSv/h). In addition, these adsorption tanks have a similar appearance with the radioactive scrap discovered by steel mills (Fig. 4A and 4B). Therefore, a new NORM contaminated industry is confirmed by this study in Taiwan, which has never been reported by the literatures.

Sample 990517 was taken from a radioactive metal imported from Hong Kong with a surface dose rate of ~45 μSv/h. Preliminary examination from the density (d~19.0) and appearance showed that this metal may be a counterbalance weight. Subsequent analysis also proved this metal block was made of depleted uranium with purity of 99.9% and $^{235}U/^{238}U$ ratio of 0.211 wt%. This value was well below the natural concentration level of 0.71 wt%, and indicated that this depleted uranium metal block was produced from the tailing of uranium enrichment process [12].

3.3. Origin of ^{60}Co contamination rebars

There are 16 discoveries of ^{60}Co contaminated rebars by steel mills since 1995. The ^{60}Co activity and trace elements concentration of contaminated rebars were summarized in Table III. The analytical results show that these rebars contain four different kinds of concentrations with regard to ^{60}Co and trace elements. It reflects that these rebars were made from four different batches of steel products. Comparison of the results in Table III with the previous study [1] also confirms that these rebars were

TABLE III. ANALYTICAL RESULTS OF ^{60}Co CONTAMINATED REBAR

Sample number[1]	^{60}Co activity Bq/g[2]	Trace element concentration, wt%				
		Cu	Ni	Mn	Cr	Si
950519	558.7	0.25	0.14	0.50	0.15	0.27
950610	5994	0.30	0.10	0.46	0.11	0.22
950619	6142	0.30	0.10	0.46	0.11	0.22
950620	6142	0.32	0.11	0.48	0.12	0.19
951223	5920	0.32	0.11	0.49	0.12	0.19
960911	5883	0.32	0.11	0.48	0.12	0.22
960923	5920	0.33	0.11	0.49	0.12	0.20
970224	5883	0.31	0.10	0.46	0.11	0.23
970310	5920	0.32	0.11	0.48	0.12	0.26
970610	5957	0.32	0.11	0.47	0.12	0.20
970925	6068	0.32	0.11	0.48	0.12	0.26
980623	5846	0.32	0.11	0.48	0.12	0.22
990210	5883	0.33	0.11	0.48	0.12	0.25
990312	6105	0.32	0.12	0.48	0.13	0.27
990512-1	37.7	0.25	0.08	0.62	0.12	0.35
990512-2	3.9	0.29	0.11	0.61	0.10	0.25

1 According to the date of discovery.

2 Corrected to the first sampling date (March 31, 1994) [1].

contaminated in the periods of October 1982 to January 1983, when the cobalt-60 sources were lost and entered the electric arc furnace. If it is true, the magnitude of cobalt-60 source was estimated to be at least 740 GBq (20 Ci) at that time by assuming 25 tons of steel produced for each batch.

4. CONCLUSIONS

Industrial origin of NORM contaminated scraps and ^{60}Co-contaminated rebars discovered in steel mills were identified by analytical results of samples combining with circumstantial evidences. Five possible industrial processes, namely oil production and treatment, heavy mineral sand benefication and rare earth processing, copper mining and processing, recovery of ammonium chloride by lime adsorption in Ammonium-soda process, and tailing of uranium enrichment process, may be involved in the production of NORM-contamination scraps. Among these, Ammonium-soda process is a new NORM contaminated industry confirmed by this study in Taiwan.

Since 1995 sixteen ^{60}Co contaminated rebars from steel mills were discovered domestically. All of them were dismantled from old buildings and were produced in the periods of October 1982 to January 1983, when the cobalt-60 sources were lost and entered the electric arc furnace. Since then, there is no other case of ^{60}Co contamination incident.

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