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"Lessons Learned" Eni Rewind on remediation projects in the presence of NORM and TENORM matrices: ISAF Gela decommissioning project

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Summary. — The case study of a dismissed petrochemical plant located in Southern Italy (Gela, CL) is presented, wherein phosphoric acid production residues - containing NORM and TENORM - have to be transformed through a series of on-site treatment procedures into non-reactive stabilised wastes, which can be accepted for disposal in a non-hazardous solid waste landfill (designed, authorized and built in ISAF's area for this specific purpose) according to the Italian regulations in force. The most relevant solutions to high complexity of technical and regulations constraints imposed by environmental consolidated text (TUA, D. Lgs. 152/2006) and radiation protection consolidated text (TUR, D. Lgs. 101/2020) both for the treatment plant and the final disposal plant are shown together with the key factors which lead Eni Rewind to start in 2022 the beginning of disposal of wastes "out of exemption" in the first authorized Italian's landfill compliance with D. Lgs. 101/2020. Objective of the Study —which has the style of a lesson learned by Eni and Eni Rewind— was to share experiences acquired during the activities carried out for the set of the first waste landfill authorised in conformity of the art. 26 of D. Lgs. 101/2020 (Authorization of waste management plants containing NORM/TENORM materials, for the purpose of disposal in the environment) and to define Guidelines with operative criteria to be adopted in similar situation all over the national and international sites managed by Eni.

1. – Introduction

Eni Rewind (Eni's environmental company) is currently responsible for the decommissioning and remediation of 3 dismissed phosphoric acid production plants located in

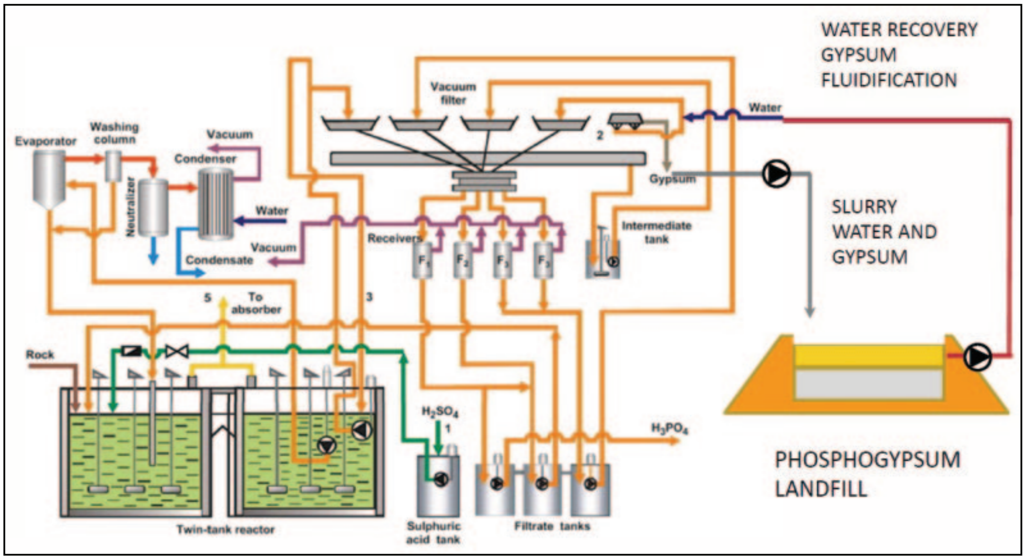


Fig. 1. – Schematic drawing of a typical Phosphoric Acid Production Plant in Italy using the Wet Process (from Decommissioning Project, modified).

3 different Italian areas. The production of phosphoric acid in Italy during the period between 1960 and 1990 occurred in two main ways: Thermal and Wet Process.

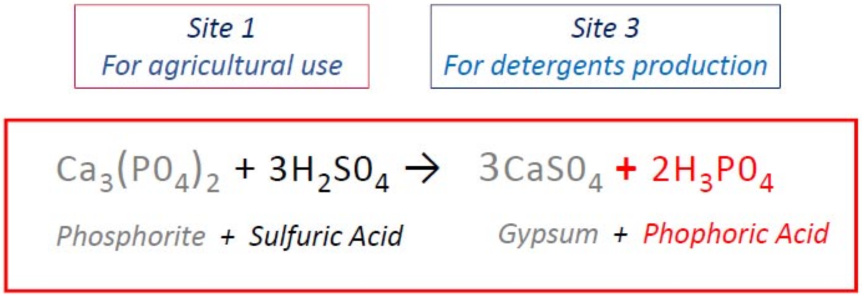
The Gela Plant was one of the sites where was performed the Wet Process (known as the Prayon process). In the following paragraph are resumed the main characteristic of the facilities and phosphoric acid production.

1˙1. *Wet Process*. – In a wet process facility, phosphoric acid is produced by reacting sulfuric acid (H2SO4) with naturally occurring phosphate rock. The industrial process can be divided in four different steps: 1) grinding and conditioning of the phosphate rock, 2) attack, or digestion, of the phosphate rock with sulphuric acid, 3) filtration, or phosphogypsum separation from the liquid fraction of phosphoric acid, and 4) washing of phosphogypsum by water. The washings are essential to obtain a high efficiency phosphoric acid in the filtration process. The objective is to obtain a phosphogypsum with a P2O5 content less than 0.5%, before it is sent to the storage sites. Figure 1 shows the schematic process of a typical Wet process Plant in Italy.

Many plants generally use a dihydrate process that produces gypsum in the form of calcium sulfate with two molecules of water (CaSO4 • 2H2O or calcium sulfate dihydrate). This one-step hemihydrate process has the advantage of producing wet process phosphoric acid with a higher P2O5 concentration and less impurities than the dihydrate process.

A simplified reaction for the dihydrate process is reported in fig. 2.

During the reaction, gypsum crystals are precipitated and separated from the acid by filtration. The separated crystals must be washed thoroughly to yield at least a 99% recovery of the filtered phosphoric acid. After washing, the slurred gypsum is pumped into a gypsum pond for storage. Water is siphoned off and recycled through a surge cooling pond to the phosphoric acid process. Considerable heat is generated in



	ID	U-238 Bq/kg		Th-230 Bq/kg		Ra-226 Bq/kg		Pb-210 Bq/kg		U-235 Bq/kg		Ra-228 Bq/kg		Th-228 Bq/kg		K-40 Bq/kg	
Dec TQ	21-45	19	3	350	53	**3186**	260	3079	463	0,9	0,1	28,8	1,6	35,9	1,1	285	12
	R21-982	199	19	955	133	**3848**	40	2834	284			23,5	1,1	36,4	1,0	289	12
	ISS21-982	15,71	0,89			2899	161			5,95	0,30	24,8	1,5	30,67	1,08	260	14
990-S7	21-65	319	25	917	130	4584	169	3167	477	14,9	3,1	38,0	2,3	44,2	1,5	236	11
	R240821A3	700	40	<387		**4121**	380	3402	341	36,0	3,8	23,7	1,2	32,9	1,0	140,0	6,0
	ISS-240821A2	216,7	12			4193	233			16,4	2,5	35,5	2,2	38,71	1,34	219	12
990-S5	21-66	880	44	794	111	4421	162	4690	700	41,4	4,8	32,2	2,0	32,5	1,2	189,9	9,0
	R260821A3	434	34	838	134	**4125**	137	5159	518	20,7	3,5	35,1	1,6	53,3	4,1	232	10
	ISS-260821A2	795	33			4300	247			48,0	4,3	27,3	1,7	28,9	1,0	156,3	8,6
	MAX	880		955		4584		5159		48		38		53		289	

Fig. 2. – Top part: schematic drawing of a typical Phosphoric Acid Production Plant in Italy using the Wet Process (from Decommissioning Project, modified). Bottom part, table 1: specific activity [Bq/kg] for solid residual sampled from Decanter 925S08 and storage tanks (S5-S7). [taken from Radiometric Risk Assessment Documents "DVRR" RADI-P-210260-RP-O-RAT-02 rev0 14/04/2022, issued for permitting procedure]

the reactor. After the treatment, the wet process phosphoric acid is used for fertilizer production (Site 1 - Wet Process), while for the use as detergent production (Site 3 - Thermal Process), it was necessary an additional treatment of purification from metals and other impurity, responsible for the production of different wastes respect the above mentioned phosphogypsum.

1·2. *Decommissioning and restoration of abandoned phosphoric acid plant in Italy.* – Remediation of some abandoned industrial areas, where phosphoric acid and its derivatives were produced in Italy, is a part of a wider sustainable development project implemented, since the early 2000s, by Eni Rewind (formerly Syndial). In these sites, obtained by Eni around the 1990s (at one time, a State Entity) from forced acquisitions, management of residues of different types containing NORM is one of the most critical factor.

Eni Rewind is Eni's environmental company which operates according to the principles of the circular economy to give new life to land, water and waste through efficient and sustainable remediation and revaluation projects. In this context, RADI, the Eni Radiation Protection Unit, provide its expertise in all activities where radiation protection studies and assessments are required.

The decommissioning of the phosphoric acid production facilities raised the issue of final disposal of residues, that originated before the cessation of the production activities.

In particular, as above mentioned, such residues are represented by liquid and solid wastes for the Wet Process and by metasilicate rocks and fly ashes for the Thermal Process. The firsts are markedly acidic (pH < 3.5), contain naturally occurring radionuclides, such as 238U, 226Ra and 232Th and are characterised by a significant concentration of fluorides, chlorides, phosphates, sulphates and heavy metals; the seconds containing respectively 226Ra (+ Iron, Phosphorus, others elements) and 210Pb and 210Po (+ phosphatic sludge and different depositions).

Considering the above, the production residues could be classified as hazardous wastes and, hence, the development of adequate on-site treatment procedures were requested to stabilize the different types of original waste, in order to obtain "non-reactive stabilized wastes", characterized by long-term stabilization and suitable for disposal in a non-hazardous solid waste landfill according with the criteria of the Italian Decrees D.M. 27/09/2010 and D.M. 24/06/2015, now updated and merged into Legislative Decree 121/2020. Also in this case, due to the lack of established protocols for the execution of the geotechnical tests, Eni Rewind and Politecnico di Torino carried out during 2019-2020 the experimental procedures and the results interpretation that led to a thorough characterisation of the residues mechanical behaviour, which is needed in order to improve and optimise the waste placement and compaction phases, the safety during landfilling activities, the mechanical stability of the waste body, the volume capacity of the landfill and the final closure envisaged by the project (Manassero and Shackelford, 1994; Dominijanni *et al.*, 2021).

1˙3. *The Radionuclides presence* . – The wet production process of phosphoric acid uses natural phosphorites which contain natural radionuclides from the Uranium-238 series and the Thorium-232 series as starting minerals.

The mentioned residues deriving from the wet process and containing traces of naturally occurring radionuclides are markedly acidic (pH < 3.5) and are characterised by a significant concentration of fluorides, chlorides, phosphates, sulphates and heavy metals. Due to the high concentration of these substances, the production residues were classified as hazardous wastes and, hence, the development of adequate on-site treatment procedures was required in order to stabilise the original hazardous waste streams and to obtain non-reactive stabilised wastes, which are able to maintain their stability even in the long term and therefore are suitable for disposal in a non-hazardous solid waste landfill according to the Italian Decrees (D.M. 27/09/2010 and D.M. 24/06/2015, now updated and merged into Legislative Decree 121/2020).

Some data, coming from radiometric characterization of matrix sampled with control bodies (ARPA) from plant area (Decanter 925S08 and storage tanks, S5 and S7), are shown in table 1. For each radionuclide are shown the results of intercalibrations performed between public laboratories (ISIN; ISS), private laboratories (Labanalysis, Chelab, Protex) and Eni (RADI). The table is taken from the documentation issued in 2021-2022 according to D. Lgs. 101/2020 for the authorization of landfill operation.

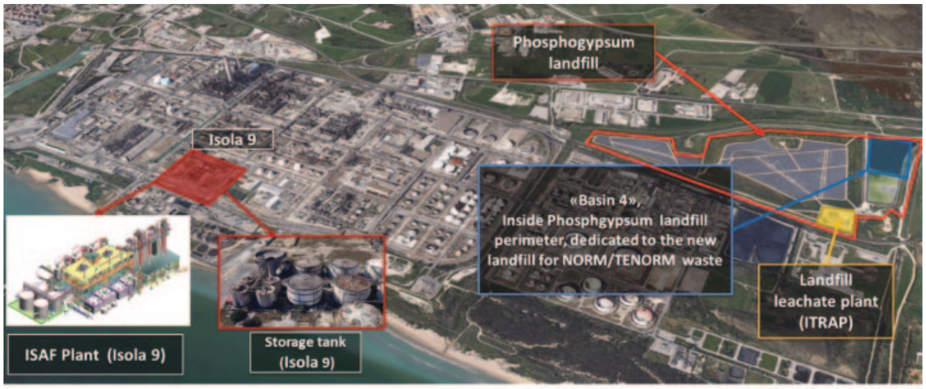


Fig. 3. – Localization of the various facilities pertaining to the plant.

2. – The ISAF Decommissioning Project

The industrial facilities (plant, storage and service tanks, pipelines etc.) are object of a complex decommissioning project called "Decommissioning ISAF" started in 2013 with the specific environmental and radioprotection permitting procedure for the removal and treatment of the residual contained in the industrial facilities, containing NORM and TENORM matrices, to be definitively stored —as the other materials from facilities demolition— in a suitable and dedicated new landfill inside the wider perimeter of the formerly mentioned Phosphogypsum Landfill, in Gela (CL).

The Decommissioning is divided in 4 different phases, resumed below, which are interconnected among them.

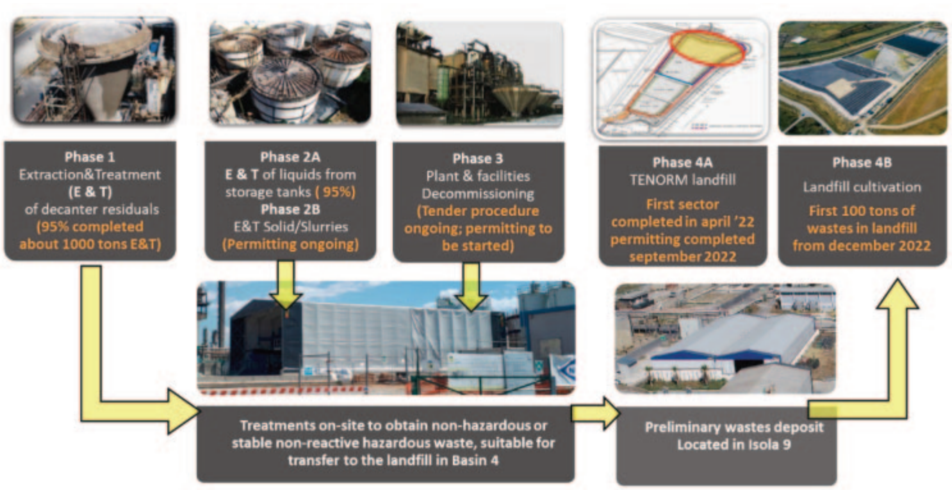


Fig. 4. – Synthesis of the objectives of the 4 Phases concerning the decommissioning of the Plant and the construction and execution of the Landfill for the disposal of NORM and TENORM wastes.

In the present paper we would like to focus in particular the Phase 4 of the project, which shows how Eni Rewind has tackled and solved the most relevant problem and find the solutions to high complexity of technical and regulations constraints imposed by environmental consolidated text (TUA, D. Lgs. 152/2006) and radiation protection consolidated text (TUR, D. Lgs. 101/2020). Both for the treatment plant and the final disposal plant are shown together with the key factors which lead Eni Rewind to start in 2022 the beginning of disposal of wastes "out of exemption" in the first authorized Italian's landfill compliance with D. Lgs. 101/2020.

The complex and inter-related authorization frame has been managed by Eni Rewind with a collaborative approach between the technical members of the Technical Committee and the Municipal/Regional/National Authorities responsible for issuing permits.

Several "external" technical meeting has been carried out after the formal session of the permitting procedure, stimulating and accelerating —separately and properly— the clarification, evaluation and solving of technical elements in a technical context less formal than the official conference but as rigorous and demanding as the institutional conference must be. In this way in the succeeding conference almost all the technical elements were successfully managed toward the final collective approval and permits issuing.

The other key factors who helped Eni Rewind to get the appreciation of Technical Committee and Authorities Responsible to issuing permits are related to the "scientific approach" and the thorough collaboration with public control bodies (*e.g.*, ARPA Agencies) for area monitoring and sampling of essay on filed from plant facilities and tanks.

3. – The technical approach for environmental monitoring and control of contaminants during decommissioning and the construction and execution of the Landfill

The problems faced in over 3 years of work and the approach followed to define the working methods shared with the control bodies for the sampling and analysis activities of the various matrices containing radionuclides in the Gela site, could be summarised as follows:

1) absence of a consolidated and standardized methodology for sampling;

2) incomparability of analytical results between third-party laboratories affiliated with Eni and public bodies (analytical methods, parameters and different data processing, non-aligned MDA, etc.);

3) different approach of the control bodies involved in the reclamation activities (ISPRA, ARPA, Prefecture, ISS) between the various sites;

4) lack of knowledge about the matrix concerning the sampling and analytical methodological approach.

All this led to the awareness of the need to establishment of a Technical Table at ISIN (National Inspectorate for Nuclear Safety and Radiation Protection) with the involvement of both public control bodies such as: ISS (Istituto Superiore di Sanità), ARPA (Agenzia Regionale Protezione Ambiente), INAIL (Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro), and Eni's Laboratories (Eni Rewind, Eni RADI and laboratories affiliated with Eni).

Following the establishment of the Technical Table, it was possible to define and agreed on the sampling procedures for the different matrices and to identify the analytical profiles to be applied to the various matrices, also through the intercalibrations performed between public laboratories (ISIN; ISS), private laboratories (Labanalysis, Chelab, Protex) and Eni (RADI) for each of the reference matrices.

All the performed work allowed to Eni not only the preparation of procedures and operating instructions for sampling, analysis and monitoring of analytical data, differentiated by matrix, but also to issue the Radiometric Risk Assessment Documents (DVRR) prepared by Radiation Protection Experts for the specific decommissioning Phase, in order to assure the physical radioprotection surveillance of the workers involved in each Phase of the decommissioning.

3˙1. *The study carried out with Politecnico di Torino*. – The study —performed by Department of Structural, Geotechnical & Building Engineering of Politecnico di Torino— considered both the treated wastes deriving from Phase 1 and the wastes taken from the L1 basin, subjected to the Treatment Procedures developed by Eni Rewind. According to the treatment procedure, the wastes has been subjected to a process of neutralization (achieved by mixing the residue with an aqueous suspension of hydrated lime until a pH value equal to 10.2 was obtained at equilibrium) and stabilisation through the addition of 0.1% by weight of Actifluo, a commercial product containing the coagulant Aluminum polychloride for the removal of fluorides from the pore solution, 10% by weight of powdered sodium bentonite and 3% by weight of Portland cement 32.5.

A testing programme was defined with the aim to evaluate the effectiveness of the treatment procedures described below, in achieving long-term chemical and mechanical stabilisation of the hazardous wastes. Such a testing programme was divided into a first stage that simulated, at the laboratory scale, the treatment procedures which are planned to be performed during the decommissioning of the production facilities, with the purpose of obtaining representative samples of the stabilised residues, and a second stage that allowed conformance of the stabilised residues with respect to the requirements for disposal in a non-hazardous solid waste landfill to be verified. In addition to the chemical conformance tests, a series of geotechnical tests were carried out in order to ascertain that the stabilised residues show "adequate physical stability and load capacity", as well as a "long-term leaching behaviour that is not subject to negative alteration in the landfill disposal conditions" (D.M. 24/06/2015, updated and merged into Legislative Decree 121/2020).

Oedometric compression, triaxial shear, torsional ring shear and column leaching tests were carried out with the aim to determine the strength and deformability parameters of the stabilised residues, as well as to investigate the long-term mobility of water-soluble contaminants under a confining stress level that simulates the final disposal conditions. Such a characterisation of the coupled chemo-hydro-mechanical behaviour allowed the effectiveness of such treatment procedures in producing a waste stream that does not pose threats to the landfill geotechnical stability to be ascertained.

The results of the study shown that, in light of the elasto-plastic work-hardening model proposed by Manassero and Shackelford (1994) with a view to describe the stress-strain response of structured particulate materials, the stabilised industrial residues showed a ductile-softening behaviour, which is typical of porous media with weak cementing bonds and initial density higher than the value corresponding to the critical state. Such a mechanical behaviour, which resembles that of heavily overconsolidated soils, allowed undrained instability phenomena that may occur in high water content treated sludges to be excluded (Arroyo *et al.*, 2006; Gens, 2019). Indeed, as a consequence of the open skeletal and highly porous microstructure, high water content treated sludges may be prone to exhibit large compressive volumetric strains upon collapse of the fragile bonds, and to accumulate positive excess pore pressures under undrained conditions until a complete loss of shear strength is reached.

Besides the chemical conformance tests, which consisted in leaching tests for quantifying the release of water-soluble compounds and the acid neutralisation capacity in accordance with standardised methods, the column leaching tests also allowed the gradual decrease in the release of contaminants to be ascertained, until a stable steady-state condition was reached in all cases. As a result, the performed tests have shown a stable behaviour of the treated residues in the long term (Dominijanni *et al.*, 2021).

4. – Conclusion

The Methodological approach derived from ISAF experience should be extended to all sites and all matrices and consisting of 2 distinct phases:

Phase 1: Methodology Development

- [1A] definition of sampling methods
- [1B] organization of sampling strategy and sample collection jointly with public control body (ARPA)
  - [1B1] homogenization and preparation of the sample "as it is" for characterization analysis
  - [1B2] definition of the "Procedure Treatment" in collaboration with Eni experts
- [1C] intercalibration between Laboratories
- [1D] discussion on the obtained results and definition of the standard procedure to be used for the investigated matrix.

Phase 2: Field Application

- [2A] definition of the protocol for sample collection and analysis during decommissioning/remediation;
- [2B] execution of routine analyses by the intercalibrated Eni's laboratories and laboratories affiliated with Eni;
- [2C] periodic cross-analyses of some samples with the Institutional Laboratories
- [2D] checks and controls on field by ARPA of the correct application of the treatment procedures and remediation/decommissioning activities;
- [2E] production of "control chart" with critical parameters showing the data trends of the reclamation processes to be shared with the Control Bodies.

In everyone's interests the next objective of the technical working group of Eni Rewind and Eni RADI with ISIN ISS ARPA ISPRA and the accredited laboratories is to make use of the operational experience of the construction sites for environmental remediation and decommissioning activities managed by Eni Rewind to develop possible new technical criteria useful for the legislator to deal —where possible in the TENORM field— with the radiation protection issue in a more accessible and standardized way, a bit like what was done for environmental legislation with the definition of the contamination threshold concentrations (CSC).

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