Contaminated Waste Minimisation Using Chemical Extraction Technology - 14316

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ABSTRACT

Radioactively contaminated material is expensive to remediate, and for transport and disposal. Innovative decontamination technologies that reduce the volume and concentration of radiological waste materials are highly desirable. Field and laboratory testing of the TechXtract® process evidences the ability to decontaminate radiological, organic and inorganic materials from a variety of substrates, whilst producing minimal volumes of secondary waste. The adaptability of the TechXtract® process to decontaminate without damage to the substrate is demonstrated using pre- and post-decontamination analysis.

INTRODUCTION

Chemical decontamination technologies are used across the nuclear industry. TechXtract® is a patented, sequential chemical extraction process developed to remove radionuclides, PCBs, and other hazardous organic and inorganic substances from solid materials such as concrete, brick, steel, and exotic metals. The technology uses multifarious task-specific chemical formulations, and engineered applications, to achieve surface penetration and removal of the contaminants from the atomic voids of metals and other substrates, or the capillaries and gel pores of concretes.

Background

In their Reference Guide [1], the EPA tabulate existing decontamination technologies by general group, listing both chemical and physical techniques. The report describes the restrictions indicated above in terms of safety, surface limitations, substrate damage and waste generation. To example these considerations, TABLE I below indicates these considerations inherent with the application of available chemical decontamination technologies.

TABLE I. Limitations of Other Chemical Decontamination Technologies [1]

Technology	Noted Adverse Factors
Alkaline Phosphates	Generate high waste volumes.
Corpex	For spray and wipe Decon, not flushing.
Corpex 921	Waste concerns related to potassium permanganate oxidant.
Fluoroboric Acid (DFD or DFD-X if used with oxidiser)	Needs further development to reduce waste. Very hazardous chemical - numerous handling/toxicity issues. Expensive to purchase and difficult to neutralize and treat. Aggressive action of fluoroboric acid is difficult to control.

Formic Acid	Mid-scale as a decontamination reagent.
Hydrogen Peroxide	Efficacy may improve as a two-step decontamination. Needs careful risk assessment.
LOMI	Generates more waste than other equivalent processes.
Nitric Acid	Does not penetrate the passivation layer, relatively ineffective. Protocol-related waste issues.
Nitric/ Hydrofluoric	Limited adoption due to health concerns.
Nitric/Sulphuric Acid	React violently with organics. Significant handling hazards. Incompatible with systems containing oil.
Nitric Permanganate	Used alongside LOMI. Needs to be repeated twice to obtain optimum levels.
Nitric/Oxalic	Limited solubility of oxalic acid.
Oxalic Acid	Residues require additional decontamination.
Oxalic Peroxide	It is a strong oxidizing agent and is not recommended in the presence of oil.
Phosphoric Acid	Handling hazards and waste issues.
Tartaric Acid	Least effective organic acid in tests.
Turco 4502	No longer distributed. Not as effective as NP, high waste as per any AP process.
Turco ARR	AP process - High Sodium waste.
Water	Ready removal of caesium but other contaminant removal limited

The TechXtract® process is an adaptable chemical decontamination process which is customised to decontaminate a broad range of radionuclides, organic and inorganic compounds from both the surface and subsurface of porous materials such as steel and concrete, whilst producing minimal secondary waste.

Decontamination techniques are largely defined in terms of chemical and physical properties. Physical techniques are effective at surface level, can be applied where damage to the substrate is not limiting and often generate significant waste volumes [2]. Many chemical techniques are similar, with additional issues including significant health and safety risk considerations and waste stabilisation and disposal [3].

Brookhaven National Laboratory determined that the following factors must be considered when selecting a technology for application under a decontamination project associated with a nuclear facility [4]:

- Radionuclide type and form
- Decontamination objective
- Material(s) requiring decontamination
- Depth and level of contamination
- Final contamination goal
- ALARA principles
- Complexity of the technology
- Volume and treatment of secondary waste
- Cost

The TechXtract® process uses controlled chemical reactions in successive steps to remove contaminants from the surface and subsurface of materials such as metal and concrete.

TechXtract® successfully targets radiological contaminants and organic and inorganic chemicals (e.g. PCBs) individually or as combined waste. Specifically designed chemical formulas penetrate below the surface into substrate voids to take out contamination and prevent leach back [5].

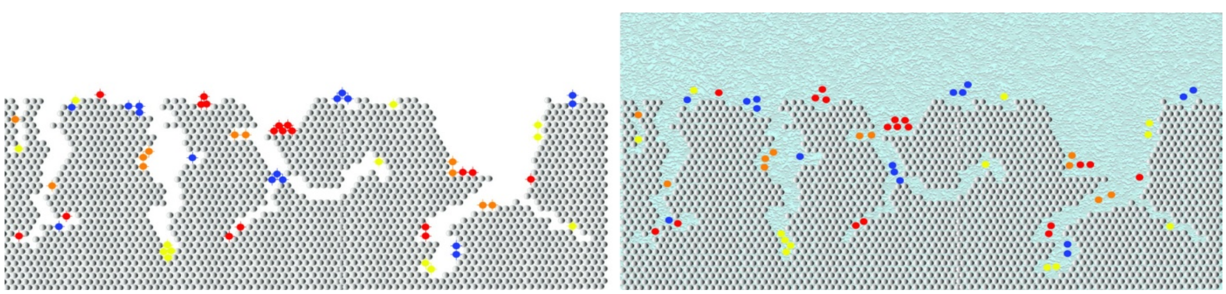
This paper considers 3 example projects that demonstrate the ability and efficacy of TechXtract® as a viable methodology for the decontamination of a variety of substrates and contamination whilst minimising secondary waste arisings.

TECHNOLOGY

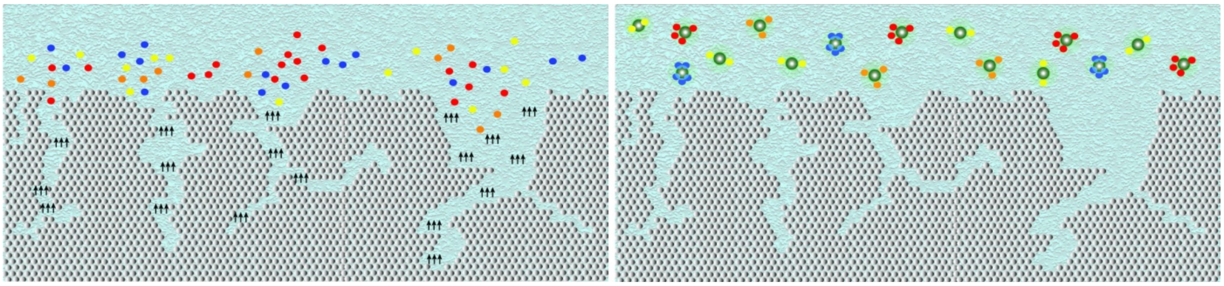
The TechXtract® chemistry uses specifically designed chemical formulas, penetrating below the surface to remove contaminants which have leached into the substrate. It is based on the hypothesis that contaminants migrate along grain boundaries and into pores (Kirkendall effect), even for seemingly non-porous media. TechXtract® solutions also address the consideration that time and secondary forces often drive contaminants to deeper levels in the substrate.

TechXtract® preparations contain macro- and micro- emulsifiers, electrolyte, flotation reagents, wetting agents, buffered organic and inorganic acids and sequestering agents. These are formulated to act at a molecular level to reopen/penetrate pores, break bonds holding contaminants and capture the contaminants in solution, as per the illustration in Figure 1[6].

The mechanisms below in Fig.1, also produce carbonic acid, a surfactant which is specifically generated to further lower the interfacial tension and enhance subsurface penetration. These (and other undisclosed) processes are integral to the design of TechXtract® and specifically target deep-set contamination, such as Tritium.



Contaminants bonded to deep in voids   TechXtract® breaks electrostatic bonds



Flotation Chemistry lifts contaminants   Contaminants complexed into solution

Fig.1 TechXtract® process illustration

Fuchs[7] identifies that if insoluble solids are adhered along the length of an orifice such as a pore, the removal mechanism nearly always involves the delivery of mechanical energy to assist in overcoming the cohesive forces at play. Where suitable, TechXtract®'s performance is enhanced by utilising ultrasonic baths, as the heat and kinetic energy generated by ultrasonics increase both surface volume and solubility to aid the extraction process [8]. If application of ultrasonics is not possible, kinetic energy can be applied through surface scrubbing.

In addressing the diffusion control aspect of leach back, it should be noted that the TechXtract® process is designed to operate using a number of applications. Each application involves sequential treatment using the formulations with mechanical agitation, a dwell period, a rinse and, where required, vacuuming. The number of applications used in a given situation depends on contamination levels, difficulty of removing contaminants from matrix and depth of contamination [9].

Dwell times (i.e. the period for which the chemicals remain in contact with the surface), during each application can also be enhanced to maximise leaching mechanism parameters and ensure optimal contaminant removal. It should be noted that overall component surface configuration (and decontamination target objectives) influence dwell times and number of applications required.

The TechXtract® decontamination solution is provided as a fully managed service. The type of contamination determines how the TechXtract® process is applied. For example, on large surface areas, such as concrete, our specialist operators apply each sequential chemical formulation as a fine mist which is mechanically agitated, allowed to dwell for a determined period, rinsed and vacuumed. On smaller targets, the TechXtract® decontamination process enhancement via ultrasonics, reduces dwell times and increases throughput.

Contaminant levels are reduced by up to 90% per application. Waste is neutralised then stabilised using grouting or absorbent polymer. The waste product can also be incinerated.

TechXtract® is most frequently the best solution when one or more of the following conditions prevail:

- Multiple contaminants are to be removed in one process
- Other methods are ineffective due to leach back and depth of contamination

- The residual contamination level required is very low (e.g. for safe re-use of item)
- The item has a high scrap/re-use value
- Waste minimisation objectives require a high volume of free release and very low volume of contaminated materials
- There are Health and Safety or engineering constraints limiting the use of alternative methods (e.g. flammability, airborne contamination, toxic/explosive gases or corrosivity)
- The contaminated surface is a challenging configuration (e.g. equipment such as valves, internal pipework)

Actual volumes of TechXtract® required depend on project parameters (e.g. surface configuration, contamination type). A typical example of volume for projects involving concrete is 120ml per square foot, per solution, per pass (with generally up to three solutions and three passes). For steel, the volume required will be less however, it is important in any application that the substrate remains wet for the entire dwell period.

A number of example projects can be cited to evidence that TechXtract® can be successfully employed in a wide range of situations: more than 600 projects have been carried out to date[10]. The following paragraphs highlight studies of particular relevance to safety, contaminant applicability, subsurface compatibility, and minimal waste outcome.

To address the requirement for safety in its application as a decontamination technology, TechXtract® formulations [11]:

- Satisfy OSHA Section XVIII, 29 CFR 1910.120
- Contain no hazardous components with respect to flammability or reactivity (40 CFR 261)
- Are designed to prevent the release of harmful fumes
- Are non-corrosive
- Operate at low and high pH blends but have a disposal pH approaching 7
- Do not contain components that would classify the solutions as hazardous for disposal under TCLP testing
- Allow the waste stream to be characterised based on extracted contaminants only
- Have non-RCRA base chemistry

In evidencing removal of PCBs, reference is made to work carried out in both the USA and the UK. TechXtract® is noted in the Superfund Innovative Technology Programme Annual Report [12] as having reduced surface PCB concentrations by 99% in a demonstration at the Pearl Harbor Naval Complex. Furthermore, consistent success in achieving PCB decontamination targets in the USA has resulted in full release of the technology by the EPA i.e. no requirement for constraints involved in obtaining a variance with ongoing monitoring [12].

Example 1: Uranium Decontamination at the Paducah Gaseous Diffusion Plant, Kentucky.

In May 2013 Matom Ltd undertook a feasibility study at the Paducah Gaseous Diffusion Plant in Kentucky, USA to demonstrate TechXtract's® ability to remove various uranium isotopes and traces of Tc-99 from a variety of metallic legacy components, some of which had been buried in the ground for over a decade.

Preparation of the chemistry and definition of the application process were undertaken before site attendance, based on information supplied by the site.

Target levels of activity for these items was <5000dpm (Disintegrations per Minute) per 100cm^2

Artefacts to be decontaminated (that were representative of the larger components) were:

1. Razor knife
2. Steel shear tooth with 3 threaded holes (approximately 12 x 4 x 2 inches)
3. Steel shear tooth with two pins (approximately 12 x 4 x 2 inches)
4. Flat twisted scrap metal plate ~10 x 3 x ¼ inches with weld areas along sides
5. Large bolt (10 x 1 inches)
6. Large bolt ~ (10 x 1 inches)
7. Steel shear tooth with 3 recessed holes (approximately 12 x 4 x 2 inches)
8. Steel shear tooth with 2 recessed holes (approximately 12 x 4 x 2 inches)

TechXtract® Decontamination Application

In the first instance, the artefacts were rinsed using a small domestic steam generator. It was apparent that the steam generator was not really suitable for the amount of steam required (Ideally between 15 – 30 psi). In this study a small ultrasonic bath was introduced for the purpose of rinsing due to the lack of steam. Intrinsically, this supplemented the steam rinse.

After 20 minutes the items were steam rinsed, TechXtract® 0100 solution was then applied and allowed to dwell for a further 20 minutes followed by a further steam rinse. This process was repeated until target levels were achieved. The process is illustrated in Fig. 2,3,4,5.

Fig. 2. Steam Rinse

Fig. 3. Application of 0200/0300

Fig. 4. Aggravate

Fig. 5. Application of 0100

Radiation Monitoring

Health physics were in attendance taking measurements for health and safety purposes and to indicate any changes following decontamination.

TABLE II. Instrumentation

Survey Instrument	Cal Due	βϒ Factor	α Factor
Ludlum Model 12 w/ 44-9-18	9/28/2013	27.4	n/a
Ludlum Model 12 w/ 43-5	1/30/2014	n/a	10.46

Average background radiation levels were approximately 40 cpm (Counts Per Minute) beta/gamma (βϒ).

Results

TABLE III. Results

Item Number	Pre-decon DPM	Post-decon DPM
1	28,085.00	None detectable above background
2	16,878.00	None detectable above background
3	15,700.00	None detectable above background
4	117.82	None detectable above background
5	150,775.00	108,723.00
6	55,430.00	40,990.00
7	21,646.00	None detectable above background
8	12,604.00	None detectable above background

Interpretation of Results

- Items 1, 2, 3 were successfully decontaminated beyond the target level of free release in between 2.5 – 3 complete cycles.
- Items 7 & 8 were successfully decontaminated beyond the target level of free release in just 1.5 cycles.
- Item 4 was successfully decontaminated beyond the target level of free release in 4 cycles.
- All items show an overall progressive decrease in activity in line with expectations.
- Items 5 & 6 did not achieve free release. These items were particularly rusty and possibly coated in fixative. It is believed that successful decontamination would have also been achieved on these components if the chemistry was allowed to dwell for longer period and further cycles completed. Time ran out for the study, and not enough cycles were carried out on these items.

Total amount of TechXtract® used for these items was less than 500ml for 3 complete cycles on all artefacts.

Example 2: Decontamination of Specialised Engineering Component.

In 2012 Matom Ltd were tasked to improve the in-house decontamination process of a specialist engineering component with a highly complex matrix. The challenge was to develop a decontamination process which successfully removed a broad spectrum of contaminants whilst preserving the integrity of the substrate and associated welds and brazes.

The engineered component has many enclosed volumes that promote high retention probability, particularly of viscous fluids. Most compounds employed during manufacture were organic molecules; while not exhaustive the following list details the majority of solution components that a component has come into contact with during manufacture.

- Citric Acid
- Phosphoric Acid
- Non-ionic surfactants
- Mineral oils
- Aliphatic hydrocarbons
- Dielectric fluid
- Fatty acids
- Potassium salts
- Alcohol solvents (Ethanol)
- Propanol-Butyl compounds
- Petroleum distillates
- Sodium/Sulphur based soaps
- Graphite/carbon

Additionally the raised temperatures used at various points during the manufacturing process can result in ‘baked-on’ or petrified deposits forming within the component volume. Detailed analysis of post built components has revealed well adhered residues present on internal and external surfaces. Further, the finished component exhibited strong static force between metal surface and any remaining particulates. This phenomenon allows some contamination to be mobile around, over and through the component (with applied momentum) without being removed from the metallic surfaces. The more aggressive manufacturing processes also lead to the production of small, usually micro, beads of constituent metal and in some cases swarf or chips that are often retained within the component volume.

Component Materials

The current generic component design contains the following material components.

TABLE IV. Base metal (bulk material): 316L Stainless steel

Grade 316L	C	Mn	Si	P	S	Cr	Mo	Ni	N
Min	-	-	-	-	-	16	2	10	-
Max	0.03	2	0.75	0.045	0.03	18	3	14	0.1

TABLE V. Braze/Alloying material: Nicrobraz LM Grade

Grade NicroBraz LM	B	Si	Fe	Cr	Ni
Min	-	-	-	16	-
Max	0.031	0.045	0.03	18	Balance

Additionally, the following residuals from the manufacturing process can be found in trace amounts: Co, C, Al, Ti, Zr, P, S, Se. However, they can be classed as contaminants and are not desirable parts of the metal or alloy matrix.

SEM (Scanning Electron Microscope) Images of contaminated component.

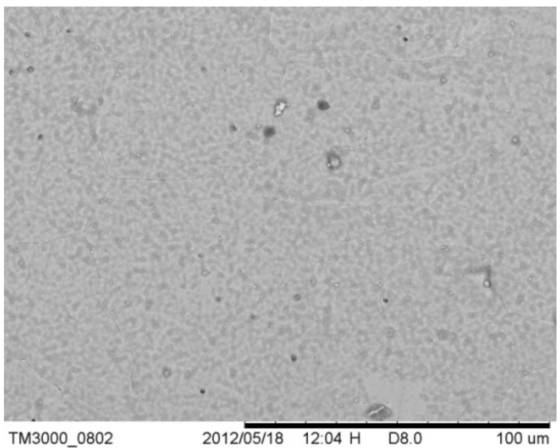


Fig. 6. Centre of matrix (x1000)

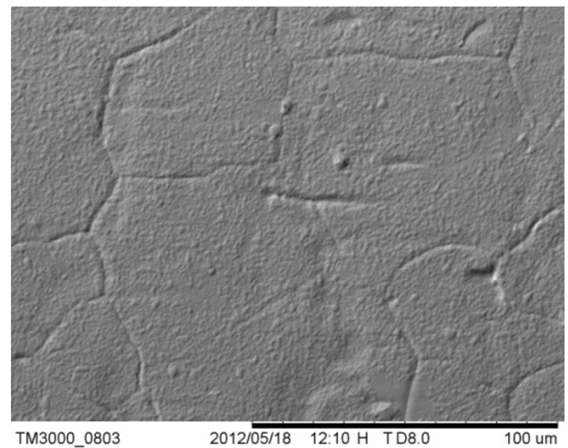


Fig. 7. Centre of matrix (Topographical) (x1000)

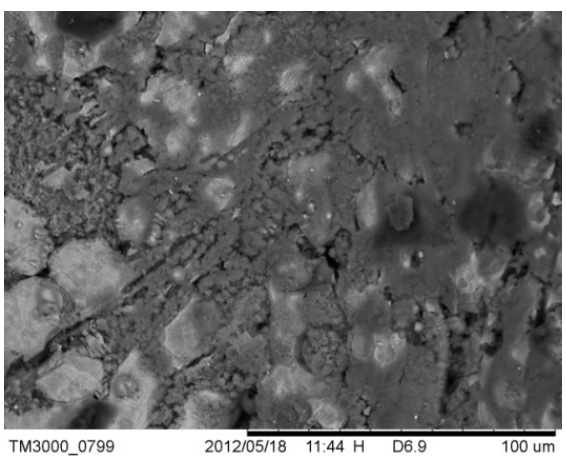


Fig. 8. Braze area (x1000)

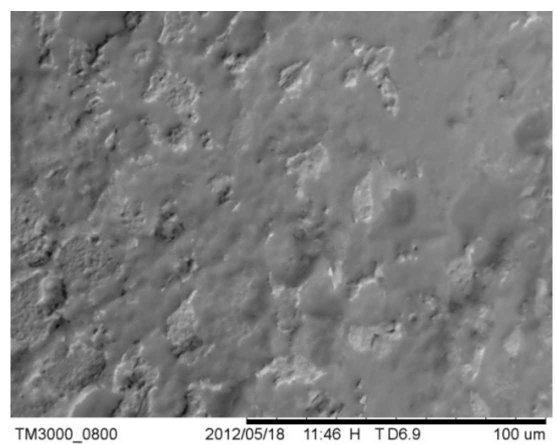


Fig. 9. Braze area (Topographical) (x1000)

TABLE VI. Semi-quantitative EDX (Energy Dispersive X-ray Spectroscopy) of Fig.6 & Fig.7

Element	Weight %	Weight % σ	Atomic %
Carbon	9.058	0.314	26.71
Oxygen	10.487	0.185	23.215
Silicon	0.546	0.034	0.689
Chromium	11.801	0.126	8.038
Iron	44.841	0.336	28.437
Nickel	8.326	0.161	5.023
Copper	3.795	0.443	2.115
Zinc	9.611	0.241	5.207
Molybdenum	1.534	0.108	0.566

TABLE VII. Semi-quantitive EDX (Energy Dispersive X-ray Spectroscopy) of Fig.8 & Fig.9

Element	Weight %	Weight % σ	Atomic %
Carbon	14.873	0.385	30.009
Oxygen	30.248	0.267	45.819
Aluminium	0.258	0.035	0.232
Silicon	3.202	0.053	2.763
Phosphorus	0.25	0.037	0.195
Chlorine	0.216	0.033	0.147
Chromium	2.826	0.071	1.317
Iron	4.795	0.099	2.081
Nickel	32.623	0.268	13.466
Zinc	10.709	0.214	3.97

Matom Ltd undertook a programme of experiments to determine the best method, TechXtract® formulation, and concentration of chemistry, to successfully decontaminate the component whilst evidencing no adverse affects to the substrate or welds and brazes.

Results

SEM Images of decontaminated component.

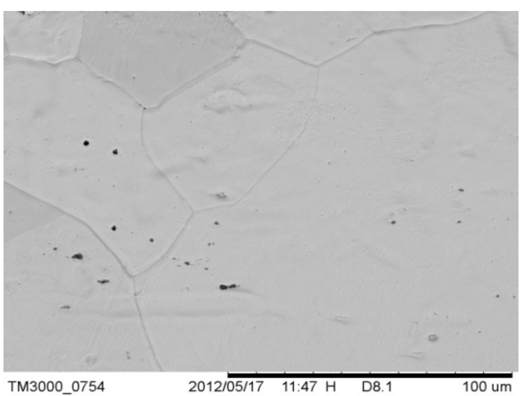


Fig. 10. Centre of matrix (x1000)

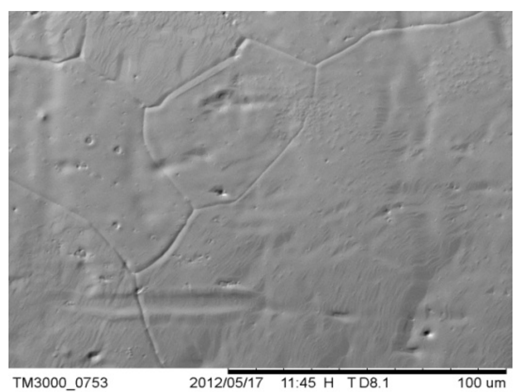


Fig.11. Centre of matrix (Topographical) (x1000)

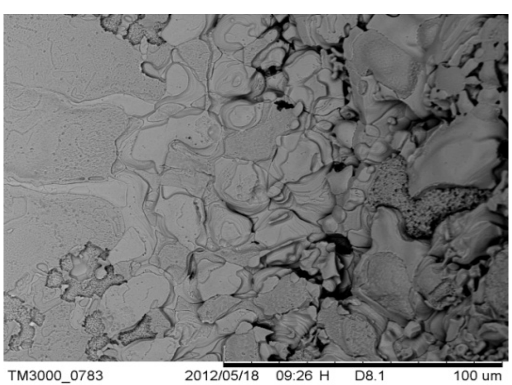


Fig.12. Braze area (x1000)

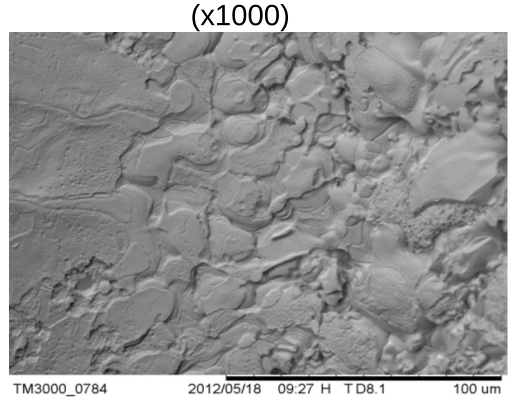


Fig.13. Braze area (Topographical) (x1000)

TABLE VIII. Semi-quantitive EDX (Energy Dispersive X-ray Spectroscopy) of Fig.9 & Fig.10

Element	Weight %	Weight % σ	Atomic %
Silicon	0.603	0.05	1.195
Chromium	17.616	0.149	18.851
Iron	66.709	0.25	66.465
Nickel	12.909	0.219	12.234
Molybdenum	2.163	0.158	1.254

TABLE IX. Semi-quantitive EDX (Energy Dispersive X-ray Spectroscopy) of Fig.11 & Fig.12

Element	Weight %	Weight % σ	Atomic %
Oxygen	1.76	0.163	5.894
Silicon	3.57	0.064	6.809
Chromium	5.812	0.091	5.987
Manganese	0.483	0.075	0.471
Iron	4.579	0.098	4.392
Nickel	83.795	0.208	76.448

During experimentation it was determined that the combination of TechXtract® and ultrasonics achieved the desired results. Complete decontamination with no adverse affects to the substrate.

Interpretation of Results

As can be seen from the results in TABLE VIII and IX the substrate materials were completely decontaminated and subsequent resulting Energy Dispersive X-ray Spectroscopy indicated that the final composition was that expected by the material manufacturer to the composition expected from the material manufacturer as shown in TABLE IV and V.

There was no adverse effects to the grain boundaries of the steel or damage to the braze area from the chemicals as shown in Fig 10 through 13.

By adapting the process to utilise ultrasonic baths, the solution can be used for multiple components before being exhausted, while additionally increasing throughput due to shorter dwell times. Volumes of TechXtract required remain minimal due to reusability of existing chemistry until exhaustion or consideration to concentrations of activity, in the instance of radiological materials.

Example 3: Decontamination of p_dioxin from Commercial Incinerator.

In November of 2012 Port Talbot and Neath Recycling Ltd, Port Talbot, UK, were forced to shut down operation of their commercial and domestic waste incinerator plant by the UK Government department, the Environment Agency, due to the high levels of p-Dioxin emissions from the exhaust system.

The exhaust system, primarily composed of mild steel, was swab tested by a certified independent laboratory at 6 points (10x10cm) within the 40m exhaust system. These swab tests were analysed for p-Dioxins and the results are shown in TABLE X:

TABLE X. p_Dioxin levels prior to decontamination.

Sample Number	Pre-Decontamination Levels (ng)
1	4.80
2	0.53
3	1.10
4	3.70
5	0.29
6	1.10

Matom Ltd performed a 3 cycle TechXtract® decontamination process throughout the incinerator exhaust system. Chemical formulation and process were determined in advance.

Results

Following the decontamination process 6 further samples were taken from the exhaust system in the proximity of the previous sample points.

TABLE XI. p-Dioxin levels following decontamination.

Sample Number	Post-Decontamination Levels (ng)
1	0.0063
2	0.0084
3	0.011
4	0.014
5	0.016
6	0.0078

TABLE XII. Results of decontamination.

Sample Number	Pre-Decon Levels (ng)	Post-Decon Levels (ng)	Reduction/efficiency
1	4.80	0.0063	99.87%
2	0.53	0.0084	98.42%
3	1.10	0.011	99.00%
4	3.70	0.014	99.62%
5	0.29	0.016	94.48%
6	1.10	0.0078	99.29%

Interpretation of Results

Following the application of the TechXtract® process, the average reduction of p_Dioxin contamination was successfully reduced by 98.45% whilst the majority of the results indicate a greater than 99% overall reduction in p-Dioxin levels.

The performance of the TechXtract® process in the remediation of the p-Dioxins from the exhaust system from the incinerator enabled the aforementioned to be cleared for use by UK's Environment Agency.

Average volume of TechXtract® required was 0.05 litres per m^2 of exhaust system.

CONCLUSIONS

The results show that for substrates Stainless Steel, Mild Steel, and various other metals, Techxtract® is an appropriate decontamination process for the removal of radiological, organic and inorganic materials. We can infer from these results, and previous empirical evidence, that other similar contaminants would be removed using approximately the same formulations and control parameters.

TechXtract® removes contamination from the surface and subsurface for all types of substrate tested. Where contaminants such as radiological contaminants leach back, further studies on concrete and metal surfaces have shown that TechXtract® is successful in removing both initial and leach back contamination. Extensive empirical evidence and analysis of performance data from independent assessment reporting conclude that TechXtract® is successful where leach back of contaminants is an issue of concern with aged and porous materials.

Whilst the volume of TechXtract® solution required varies according to surface type, porosity, volume of contamination and other project requirements, TechXtract® is demonstrated to be effective on aged surfaces with minimal secondary waste arisings.

Footnotes

®TechXtract is a registered trademark of Active Environmental Technologies Inc.

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