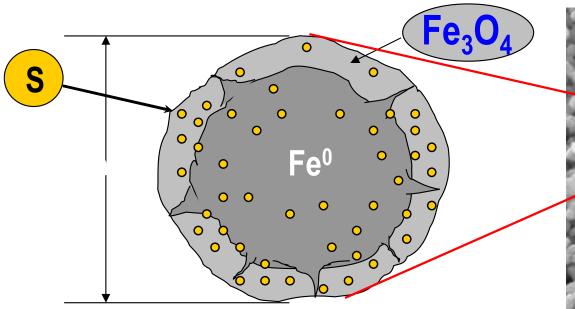
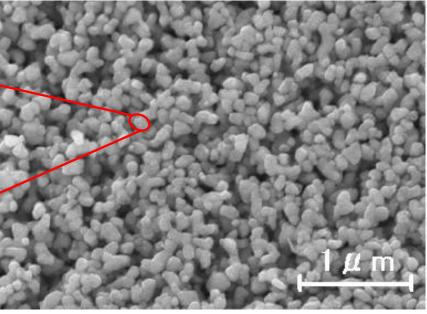
## Clean Up of Lead (Pb) contaminated Soil & Groundwater by RNIP® (Reactive Nanoscale Iron Particles)

December 2021



#### What is R N I P<sup>®</sup> ?





- Fig. 1 Schematic RNIP<sup>®</sup> structure Fig. 2 SEM image of RNIP<sup>®</sup> RNIP<sup>®</sup> consists of metallic iron core ( $\alpha$ -Fe) and magnetite shell (Fe<sub>3</sub>O<sub>4</sub>).
  - Particle size; 70 nm
  - Specific surface area;  $30 \text{ m}^2/\text{g}$



#### What is RNIP<sup>®</sup> ?

- $\succ$  RNIP<sup>®</sup> is processed in aqueous slurry.
  - Slurry Density; 1.25 g/ml
  - Solid concentration; 25 wt.%
  - Slurry Viscosity; 600~700 mPa•s
- Slurry of RNIP<sup>®</sup> is diluted by several to one hundred times in use.
  - Dilution viscosity;  $<10 \text{ mPa} \cdot \text{s} >$



**Fig. 3** Slurry of RNIP<sup>®</sup>



#### What is RNIP<sup>®</sup> ?

We have produced RNIP<sup>®</sup> slurry of 60 tons per month at our Higashi-hiroshima plant since 2017.



Fig. 4 Higashi-hiroshima plant

- Site area
   ca. 4,000m<sup>2</sup>,
   built in October 2017
- Production capacity 60 tons/month (Max 90 tons/month)

Packaging product



1m<sup>3</sup> SUS container



200L Drum can



20L Plastic container

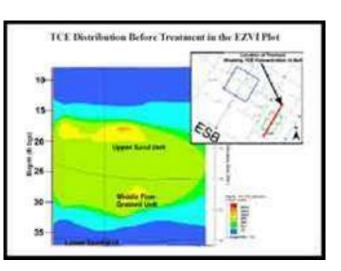


## NASA used RNIP® first in the world !

- For clean up of VOC's contaminated soil in Kennedy Space Center's Launch Complex34 November 2002.
- By Superfund Innovative Technology Evaluation program of EPA.
- NASA's Emulsified Zero-Valent Iron (EZVI) involves RNIP<sup>®</sup> into a surfactant-stabilized, biodegradable oil-in-water emulsion<sup>1)</sup>.
- Quantity of injected EZVI ; 0.4~0.8wt% based on solid
- Initial VOC's 200~6000 mg/kg  $\Rightarrow$  After clean up : ND











#### Characteristics of RNIP<sup>®</sup> summary

- RNIP<sup>®</sup> is an environmentally friendly material that is non-toxic, safe and secure. Therefore, it does not cause a secondary environmental pollution after using it.
- RNIP<sup>®</sup> has a high performance for clean up of heavy metals, such as lead (Pb), chromium (Cr), arsenic (As) and selenium (Se)<sup>2), 3), 4)</sup>.
- RNIP<sup>®</sup> has a high mobility performance in subsurface and is suited for in-situ rapid clean up works using a conventional chemical grouting method or a mechanical mixing method.
- The VOC clean up performance of RNIP<sup>®</sup> is much greater than that of commercial iron powders by 100 times<sup>5</sup>.
  NAKAMURAKISO.CO., LTD.

#### **1** Harmless materials

#### **Elution test of RNIP**<sup>®</sup>

#### **Content test of RNIP®**

Element		Elution Value of RNIP	Japanese Regulation
Cd [m	ng/l]	< 0.001	$\leq 0.01$
Total-CN [m	g/l]	Not detected	Not detected
Pb [n	ng/l]	< 0.005	$\leq 0.01$
Cr6+ [n	ng/l]	< 0.04	$\leq 0.05$
As [n	ng/l]	< 0.001	$\leq 0.01$
Total-Hg [m	ng/l]	< 0.0005	≦ 0.0005
Se [n	ng/l]	< 0.002	$\leq 0.01$
F [n	ng/l]	< 0.5	$\leq 0.8$
B [n	ng/l]	< 0.1	≦ 1
Total-Cr [m	g/l]	< 0.1	-
Mn [m	ng/l]	< 0.1	-

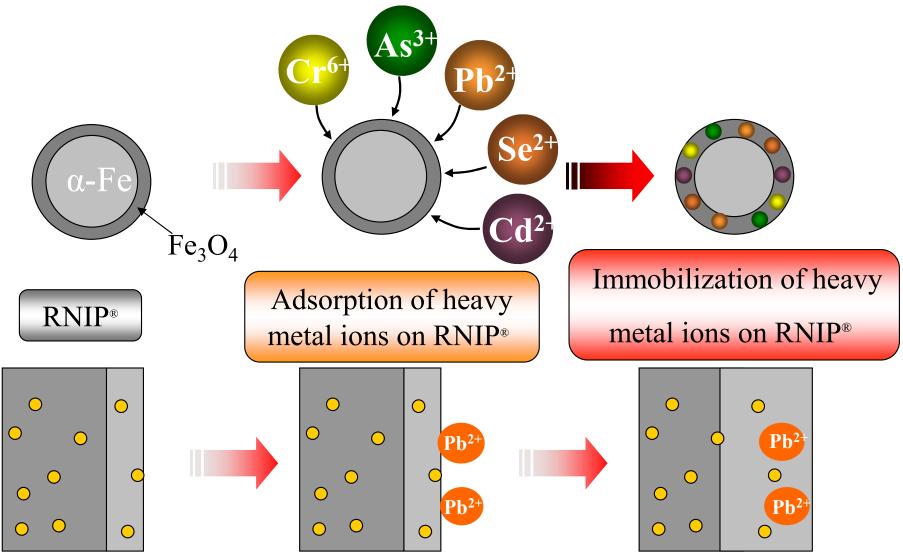
Elen	nent	Content Value of RNIP	Japanese Regulation
Cd	[mg/kg]	< 2	<b>≦ 150</b>
Total-CN	[mg/kg]	< 5	$\leq 50$
Pb	[mg/kg]	< 5	<b>≦ 150</b>
Cr6+	[mg/kg]	< 5	$\leq 250$
As	[mg/kg]	< 1	<b>≦ 150</b>
Total-Hg	[mg/kg]	< 1	≦ 15
Se	[mgkg]	< 1	<b>≦ 150</b>
F	[mgkg]	< 20	$\leq 4000$
В	[mg/kg]	< 20	$\leq 4000$

On the Ministry of Environmental Notification of No. 19 from 2003 for the contaminated soil in Japan

On the Ministry of Environmental Notification of No. 46 from 1991 for the contaminated soil in Japan

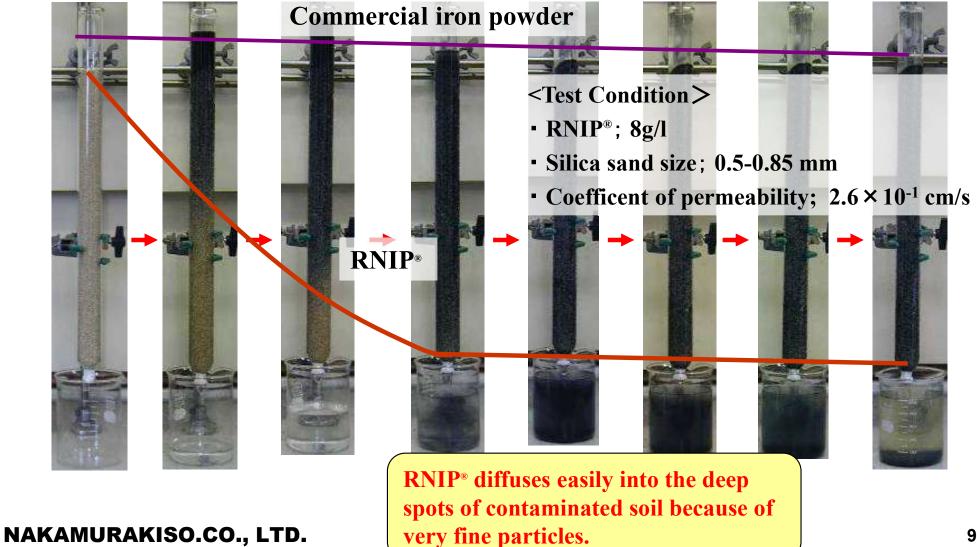


#### **(2)** Reaction schematic of clean up of heavy metals by RNIP<sup>®</sup>





#### (3) High mobility performance for in-situ clean up Mobility test with saturated soil



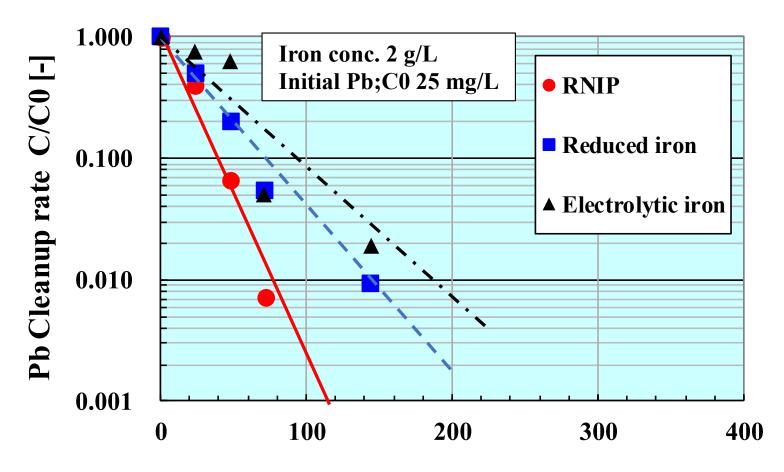
#### **③** High mobility performance for in-situ clean up works



Fig. 5 Injection of RNIP<sup>®</sup> with chemical grouting

Fig. 6 Mixing of RNIP<sup>®</sup> with mechanical mixing or agitating





Reaction time [h]

Fig. 7 Reaction time dependency of Lead cleanup rate by RNIP<sup>®</sup> compared with conventional irons<sup>2), 3)</sup>

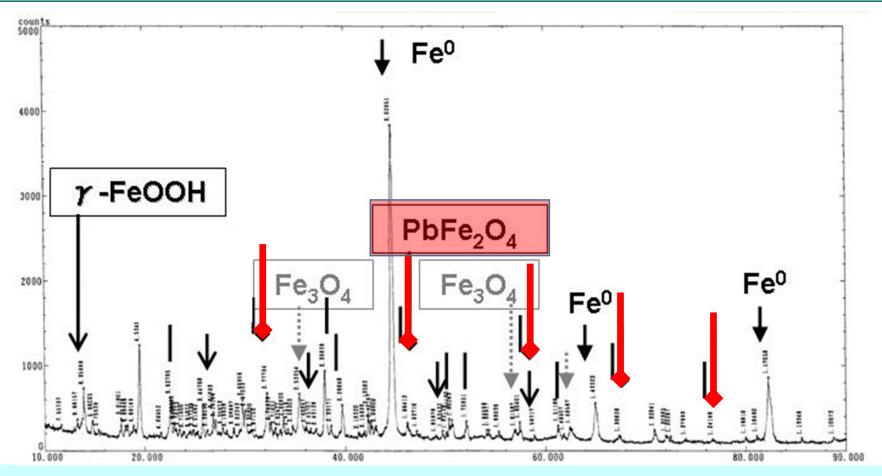
**Quite rapid cleanup of lead by RNIP<sup>®</sup> can be realized** 

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Table 1. Required quantity of RNIP® (solid)for lead cleanup level to meet Environmentalstandard Japan in 2weeks

Lead concentration<br/>[mg/L]Required quantity of<br/>RNIP® solid [g/L] $5 \sim 20$  $0.5 \sim 1.0$ 





X-Ray diffraction analysis of RNIP<sup>®</sup> on which lead immobilized indicates lead ferrite is formed on the surface of RNIP after cleanup of lead by RNIP<sup>®</sup>.

Lead ferrite has a very small, ultimately nearly zero, solubility product.



## Table 2.Leaching test results on Lead immobilizedon RNIP® by Japanese Industrial Standards (JIS)

Assay	Lead conc. In filtered solution after leaching test [mg/L]	Environmental standard, Japan [mg/L]
Acid*	< 0.005	< 0.01
Alkali**	< 0.005	< 0.01

- Reaction condition: Pb 10 mg/L, RNIP<sup>®</sup> solid 1g/L, after 21 days
- \* Acid addition leaching test method I JIS K 0102 61. 2
- **\*\*** Alkali addition leaching test method II JIS K 0102 61.2



## **Further Overseas R&D on RNIP®**

Co-operative academia-industrial R&D with Professor Dr. Volker Birke, University of Wismar, Germany, on application of RNIP<sup>®</sup> for novel cleanup technologies and an overseas market supported by the subsidy of Hiroshima prefectural government has just begun.



Professor Dr. Volker Birke

Prof. Dr. Volker Birke currently works at the Department of Mechanical, Process and Environmental Engineering, University of Wismar. Volker does research in Environmental Chemistry, Chemical Kinetics and Analytical Chemistry. Volker Birke has 30 years of experience in practical environmental chemistry, particularly in the destruction of hazardous wastes and toxic compounds in the environment. He has experience in remediation of contaminated sites, hazardous waste management, soil and ground water remediation, especially regarding permeable reactive barriers (PRBs), and in the application of innovative ex situ and in situ remediation to persistent organic pollutants such as PCBs using zero valent iron(ZVI), especially nano size ZVI. He has known much about our RNIP and has long wanted to use RNIP since before.

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Funded by



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- 1) J. Quinn et al., Environ. Sci. Technol., 39, pp. 1309-1318 (2005).
- K. Okinaka et al., Proceeding of the 14<sup>th</sup> Annual Conference of Japan Society of Waste Management Experts, Tsukuba, pp. 22-24 (2003).
- K.Okinaka et al., Proceeding of the 3<sup>rd</sup> International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, San Diego, California, pp. 144-149 (2004).
- 4) B. Laura et al., Environ. Sci. Technol., 42, pp. 2600-2605 (2008).
- 5) K. Okinaka et al., Proceeding of the 4<sup>th</sup> International Conference on Remediation of Chlorinated and Recalcitant Compounds, Monterey, California (2003).

#### <Overseas Patens>

- (1) US Patent No. 7482384.
- (2) Spanish Patent No. 1318103.
- (4) German Patent No. 1486463.
- (5) British Patent No. 1486463.



#### Acknowledgement

# Thank You for Your Warm Attention



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