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Nuclear Energy Critical Material Waste Minimization Enabled by AM Techniques

M3CR-22PN0401013

May 2024

IJ van Rooyen S Meher P Thallapally J Dos Santos C Silva SHR Shin T Wang D Garcia M Nartu QRS Miller T Hartmann



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Summary

In September 2020, the U.S. government issued an executive order to address the threat to the domestic supply chain from its reliance on critical minerals (CMs) from foreign competitors and to support the domestic mining and processing industry. The Advanced Materials and Manufacturing Technology (AMMT) program is addressing this executive order by evaluating advanced manufacturing (AM) and its impact on the demands of CMs for energy production in general and how the deployment of AM in nuclear energy will support the projected goals of the Paris Accord and further a net-zero carbon economy (NZE) by 2050. Two strategic reports were previously prepared by the AMMT program to date and identified two areas for more detailed exploration: (1) the replacement of high-risk CMs such as cobalt and niobium by more abundant minerals and (2) the minimization and utilization of CM waste streams.

From a list of 50 CMs and evaluations of the CMs related to advanced alloys selected for deployment in Gen-IV reactor systems, the following minerals were identified as most important to the nuclear industry: AI, Cr, Co, Mn, Ni, Nb, Ta, Ti, V, W, and Zr. Co is one of the CMs with a high supply risk for both short and medium terms for advanced alloys for Gen-IV reactor systems. As global demand for stainless steel rapidly increases, supplies for minerals such as nickel, manganese, and chromium become more critical. To shift peak mineral production and delay the scarcity of alloying minerals, the recycling rate of minerals needs to increase. However, the natural sources for these minerals are exhaustible, and Hubbert's model projects peak production for these minerals between 2020 and 2050. Therefore, experimental feasibility studies were identified as part of the strategy to decrease nuclear material vulnerability due to CM supply and the economic impact on the following elements: (1) Co, as a short-term (2020–2050) and medium-term (2025–2035) high supply risk, and (2) Ni, a near-critical material for the near term, but a high critical material for the medium term (2025–2035).

In this report, experimental feasibility studies show that the recycling of solid waste through the consolidation of machining chips or offcuts and liquid waste metal recovery through aqueous separation can have positive impacts for nuclear material supply risks.

The solid-state recovery or recycling of CMs involves the use of alloy shavings or machined chips as the starting materials for friction stir consolidation (FSC) to produce dense billets that can be extruded to different useful dimensions. This process shows the benefit of a full circular process, with no waste of CMs, and can be repeated several times. FSC has been considered in this work because it has been reported to be a reproducible process and can refine the microstructure without producing unwanted textures, thereby reducing anisotropy.

Three nuclear grade materials have been processed by FSC to evaluate the feasibility of this process for the efficient recovery of materials: (1) Alloy 709 (Fe–20Cr–25Ni with other minor elements such as Mo, Mn, Nb, N, C, etc.) is a 20Cr–25Ni austenitic grade stainless steel and has been considered for sodium-cooled fast reactors (SFRs). (2) Alloy 316H is a high carbon modification of Alloy 316 developed for use at elevated temperatures. The alloy is used for structural and pressure vessel applications at temperatures above 500°C and is currently considered for multiple reactor types. (3) Alloy 617 is a nickel–chromium–cobalt alloy that has many outstanding properties such as high-temperature oxidation resistance and corrosion resistance in various corrosive aqueous environments. It is the sixth material cleared by the Boiler and Pressure Vessel Code (BPVC) for use in high-temperature nuclear reactors.

In the FSC process, metal chips of all three alloys were successfully solid-state-consolidated into dense products after limited optimization of process parameters. The extents of consolidation in A709 and IN617 are higher compared to that in 316H. Further, the real-time density evolution was measured, revealing the mechanism of the consolidation process, which will allow for future upscaling benefits. In all three alloys (A709, 316H, and IN617) that were FSC-processed, the grains are refined in size and nearly equiaxed, removing any anisotropy from the starting material. In A709, the grain size decreased by nearly 80 percentage (from 10 to 2 μ m). Similarly, the grain size reduction was nearly 88 percentage in IN617 (from 10.2 to 1.2 μ m). Subsequently, the hardness of the FSC product substantially increases because of grain boundary strengthening (Hall–Petch relationship).

The development of simple and cost-effective techniques for CM production and recovery from industrial wastewater will lead to an enhancement in the current recycling rate of the minerals and reduce the potential hazards of industrial wastewater bearing high concentrations of minerals. In this project, ionic metal-organic framework (iMOF)-based adsorbents are successfully designed for CM extraction from aqueous solution. These sorbents can be integrated into electrochemical or magnetic separation approaches to meet the demands of practical applicability and commercialization. The synthesized iMOFs were characterized using various techniques to understand their physicochemical properties. The iMOFs possess chemical stability, a high adsorption capacity, and rapid mineral uptake. Specifically, the iMOFs are highly stable in aqueous solution over wide pH ranges, indicating that they are suitable for use in industrial wastewater with harsh chemical environments. The uptake properties of the iMOFs were evaluated in terms of the adsorption capacity, removal efficiency, and kinetics. The adsorption capacity of iMOFs towards nickel reaches 34.1 mg/g with a removal efficiency of >99.9%. Notably, complete removal of nickel takes place within 5 min, which is much faster compared to other adsorbents. Moreover, the iMOFs can simultaneously coextract multiple minerals, proving their effectiveness as general adsorbents.

In summary, this project provides evidence of the successful recycling of solid waste offcuts resulting from conventional manufacturing processes from three relevant alloys to next-generation nuclear reactor developers, providing a potentially upscalable circular process where no critical elements will be lost. Furthermore, iMOF-based adsorbents were successfully designed for CM extraction from aqueous solution, thereby providing a pathway for future upscaling for salvaging dissolved Ni ions. This research has achieved its goal of showing the impact of novel applications of recycling technologies for solid and liquid wastes that can be upscaled for application.

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Acronyms and Abbreviations

AM	advanced manufacturing
AMMT	Advanced Materials and Manufacturing Technology
BAU	business as usual
BET	Brunauer–Emmett–Teller
BPVC	Boiler and Pressure Vessel Code
BSE	backscattered electron
СМ	critical mineral
DOE	U.S. Department of Energy
DMA	dimethylammonium
DMACI	dimethylammonium chloride
EBSD	electron backscatter diffraction
EDS	energy dispersive spectroscopy
FSC	friction stir consolidation
FSW	friction stir welding
HCI	hydrochloric acid
ICP-OES	inductively coupled plasma optical emission spectroscopy
iMOF	ionic metal–organic framework
MOF	metal–organic framework
MMT	million metric tons
NAS	National Academy of Sciences
NZE	net-zero carbon economy
PNNL	Pacific Northwest National Laboratory
PXRD	powder X ray diffraction
SE	secondary electron
SEM	scanning electron microscopy
SFR	sodium-cooled fast reactor

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1.0 Introduction

In September 2020, the U.S. government issued an executive order to address the threat to the domestic supply chain from its reliance on critical minerals (CMs) from foreign competitors and to support the domestic mining and processing industry (DOE 2021). In this context, a national strategy on CMs was developed, which had an impact on the U.S. Department of Energy's (DOE's) vision for the decade of 2021-2031. This vision embraces science and technology to re-establish U.S. competitiveness in the CM and material supply chains by (a) scientific innovation and technologies to ensure resilient and secure CMs and maintain a domestic material supply chain. (b) building a long-term minerals and materials innovation ecosystem to foster new capabilities to mitigate CM supply chain challenges, (c) increasing private sector adoption for sustaining the domestic CM supply chain, and (d) coordinating with international partners and federal agencies to diversify global supply chains and ensure the adoption of best practices for sustainable mining and processing (DOE 2021). The Advanced Materials and Manufacturing Technology (AMMT) program is addressing this executive order by evaluating advanced manufacturing (AM) and its impact on the demands of CMs for energy production in general and how the deployment of AM in nuclear energy will support the projected goals of the Paris Accord and further a net-zero carbon economy (NZE) by 2050. Two strategic reports have been issued by the AMMT to date (Hartmann et al., 2022, 2023), and detailed experimental design and execution have been the focus of the past year's work regarding (1) the replacement of high-risk CMs such as cobalt and niobium with more abundant minerals and (2) the minimization and utilization of CM waste streams.

1.1 Background

The demand for metals and CMs will rapidly increase with international ambitions to address climate change, in which the current strategy is set up to comply with a 2°C scenario (cf. 2015 Paris Accord). Global material use will more than double, from 79 billion tons in 2011 to 167 billion tons in 2060. The projected growth in materials use, coupled with the environmental consequences of material extraction, processing, and waste, is likely to increase pressure on the resource bases of the planet's economies and jeopardize economic and social gains in well-being.

CMs are essential for a range of clean energy technologies, which are experiencing rapid growth due to global policies and business agendas in recent years. Record deployment of clean energy technologies such as solar photovoltaics and batteries is propelling unprecedented growth in CM markets, while electric car sales exceeded 10 million units in 2022. Energy storage systems experienced even more rapid growth, with capacity additions doubling in 2022 and wind power installations set to resume their upward trend. All of this has led to a significant increase in demand for CMs and increased supply pressure on all other industries. From 2017 to 2022, demand from the energy sector was the main factor behind a tripling in the overall demand for lithium, a 70% jump in demand for cobalt, and a 40% rise in demand for nickel. In 2022, the share of clean energy applications of the total demand reached 56% for lithium, 40% for cobalt, and 16% for nickel, up from 30%, 17%, and 6%, respectively, five years ago (IEA 2023).

Driven by rising demand and high prices, the market share of energy transition minerals doubled over the past five years, reaching USD 320 billion in 2022. Energy transition minerals, which used to be a small segment of the market, are now moving to center stage in the mining

and metals industry. A combination of volatile price movements, supply chain bottlenecks, and geopolitical concerns has created a mix of risks for secure and rapid energy transitions.

1.2 CMs for Nuclear Materials

The 2022 final list of CMs includes the following 50 minerals: aluminum, antimony, arsenic, barite, beryllium, bismuth, cerium, cesium, chromium, cobalt, dysprosium, erbium, europium, fluorspar, gadolinium, gallium, germanium, graphite, hafnium, holmium, indium, iridium, lanthanum, lithium, lutetium, magnesium, manganese, neodymium, nickel, niobium, palladium, platinum, praseodymium, rhodium, rubidium, ruthenium, samarium, scandium, tantalum, tellurium, terbium, thulium, tin, titanium, tungsten, vanadium, ytterbium, yttrium, zinc, and zirconium. These elements were paired with Gen-IV reactor types (Hartmann et al., 2022) (Table 1), showing the vulnerability of reactor manufacturing, sustainability, and the influence on growth potential due to material availability.

	Potential use as alloying metal in structural materials for Gen-III+ or Gen-IV nuclear reactors								
Critical Mineral	LWR	SFR	MSR	VHTR	GFR	LFR	Micro- Reactor		
Aluminum		yes	yes	yes	Yes	yes	yes		
Beryllium									
Bismuth						yes			
Chromium	yes	yes	yes	yes	Yes	yes	yes		
Cobalt		yes	yes	yes	Yes				
Graphite			yes	yes					
Hafnium	yes								
Manganese	yes	yes	yes	yes	Yes	yes	yes		
Nickel	yes	yes	yes	yes	Yes	yes	yes		
Niobium		yes	yes	yes	Yes	yes	yes		
Tin	yes								
Titanium		yes	yes	yes	Yes	yes	yes		
Tungsten		yes	yes			yes	yes		
Vanadium		yes	yes			yes	yes		
Zirconium	yes								

Table 1. Pairing of listed CMs with the alloys to be used in Gen-IV reactor types [adapted from (Hartmann et al., 2022)].

Within the next decade, commodity prices for CMs crucial for steel production will see a sharp surge since lower ore grade qualities will be mined and refined and higher volumes of orebearing rocks must be processed for comparable metal yields. The large-scale deployment of AM in industrialized countries and China, specifically within the nuclear industry, may result in significant materials and cost savings, allowing for fast prototyping, which can provide nuclear materials with superior mechanical properties and corrosion resistance. Here, the adoption of AM materials for critical parts within the nuclear industry will contribute to the economic feasibility of manufacturing processes and therefore enhance the deployment of AM materials for nuclear energy production. Estimates must be revised if the potential is considering the use of Gen-IV technology for primary energy production to reduce carbon emissions by 4,000 million metric tons (MMT). Based on the impact of supply disruption and supply risk, which is a methodology developed by National Academy of Sciences (NAS), and the importance to (decarbonized clean) energy, elements are categorized according to supply risk:

- Short-term (2020–2025) high supply risk: seven critical materials—namely, cobalt (Co), dysprosium (Dy), gallium (Ga), natural graphite, iridium (Ir), neodymium (Nd), and terbium (Tb). There are also nine near-critical (electrical steel, fluorine, lithium, magnesium, nickel, platinum, praseodymium, silicon carbide, and uranium) and seven noncritical (aluminum, copper, manganese, phosphorous, silicon, tellurium, and titanium) materials.
- Medium-term (2025–2035), there are thirteen critical materials (cobalt, graphite, gallium, platinum, magnesium, silicon carbide, lithium, nickel, dysprosium, iridium, neodymium, praseodymium, and terbium), six near-critical materials (copper, electrical steel, silicon, uranium, aluminum, and fluorine), and four noncritical materials (manganese, titanium, phosphorus, and tellurium) (Bauer et al., 2023).

From the list of 50 CMs, the focus of earlier AMMT program evaluations was the CMs related to advanced alloys selected for deployment in Gen-IV reactor systems. Among the minerals identified as most important to the nuclear industry (e.g., Al, Cr, Co, Mn, Ni, Nb, Ta, Ti, V, W, and Zr for advanced alloys for Gen-IV reactor systems), cobalt (Co) is one of the CMs with a high supply risk for both short and medium terms (Hartmann et al., 2022).

Stainless steel, an iron–carbon alloy with nickel (Ni), manganese (Mn), and chromium (Cr), is one of the most important materials in the world. Owing to its excellent properties such as resistance to corrosion, ductility, and toughness, stainless steel has been widely used in many industrial applications. As global demand for stainless steel increases, supply for Ni, Mn, and Cr becomes more critical. However, the natural sources of these minerals are exhaustible, and Hubbert's model projects peak productions for the minerals between 2020 and 2050 (Figure 1) (Sverdup and Ragnarsdóttir 2014).



Figure 1. Production curves for (a) Mn, (b) Cr, and (c) Ni using Hubbert's model and the system dynamics STEEL model (Sverdup and Ragnarsdóttir 2014).

A shortage of the minerals in supply can be mitigated by recycling minerals. It has been reported that the time for mineral scarcity can be significantly delayed depending on recycling rates (Table 2) (Sverdup et al., 2013). For example, Ni and Mn have burn-off times of less than 45 years with current recycling rates, and the burn-off time can be delayed to more than 400 years with 90% improved recycling rates. Enhanced recycling is essential to shift CM peak production and delay the scarcity of alloying minerals.

Table 2.	Estimated burn-off times for minerals depending on different improved recycling rates
	in the market. BAU = business as usual with recycling as today. All values are years
	counted from 2010 and forwards (Sverdup et al., 2013).

Element	BAU	50%	70%	90%	95%
Iron	79	126	316	316	632
Aluminium	132	184	461	461	921
Nickel	42	42	209	419	838
Copper	31	31	157	314	628
Zinc	20	37	61	61	123
Manganese	29	46	229	457	914
Indium	19	38	190	379	759
Lithium	25	49	245	490	980
Rare Earths	455	864	4,318	8,636	17,273
Yttrium	61	121	607	1,213	2,427
Zirconium	67	107	533	1,067	2,133
Tin	20	30	150	301	602
Cobalt	113	135	677	1,355	2,710
Molybdenum	48	72	358	717	1,433
Wolfram	32	52	258	516	1,031
Tantalum	171	274	1,371	2,743	5,486
Niobium	45	72	360	720	1,440
Helium	9	17	87	175	349
Chromium	225	334	1,674	3,348	6,697
Gallium	500	700	3,500	7,000	14,000
Germanium	100	140	700	1,400	2,800
Titanium	400	400	2,000	4,000	8,000
Tellurium	387	387	1,933	3,867	7,733
Antimony	25	35	175	350	700
Selenium	208	417	5,208	10,417	20,833
Gold	48	48	71	357	714
Silver	14	14	43	214	429
Platinum	73	73	218	1,091	2,182
Rhodium	44	44	132	660	1,320
Uranium	61	119	597	5,972	11,944
Phosphorus	80	128	640	3,200	6,400
Legend, yrs	0-50	50-100	100-500	500-1,000	1,000-5,000

Enhancements in quality and yield of CM recycling and the recovery of CMs from solid and industrial waste streams are needed to enhance supply security for stainless-steel production and to shift the time to scarcity for society to future years to achieve an NZE by 2050.

1.3 Strategy for Decreasing Nuclear Material Vulnerability Due to CMs

Figure 2 shows a schematic of the CM strategy for nuclear materials as developed in previous work (Hartmann et al., 2022). As a part of the U.S. DOE's focus on CMs, increasing manufacturing efficiency, identifying better substitutes, and improving the recycling and recovery of CMs are important aspects that need focus using both experimental and computational efforts. Experimental feasibility studies were identified as part of the strategy to decrease nuclear material vulnerability due to CM supply and economic impacts on the following elements: (1) Co, as a short-term (2020–2050) and medium-term (2025–2035) high supply risk, and (2) Ni, a near-critical material for near term, but a high critical material for the medium term (2025–2035).

Figure 2. Schematic of the CM strategy for nuclear materials as developed during this study.

1.4 Scope of This Report

In this report, experimental feasibility studies are presented. These studies show that the recycling of solid waste through the consolidation of machining chips or offcuts and liquid waste metal recovery through aqueous separation can have positive impacts for nuclear material supply risks. The use of novel methods to separate and recover CMs from solid and liquid industrial waste streams is needed, which supports the goal of enhancing the quality and yield of CMs.

2.0 Solid Waste: Recycling through the Consolidation of Machining Chips or Offcuts

In this study, the solid-state recovery or recycling of CMs involves the use of alloy shavings or machined chips as the starting materials for friction stir consolidation (FSC) to produce dense billets that can be extruded to different useful dimensions (Figure 3). This process shows the benefit of a full circular process, with no waste of CMs, and can be repeated several times. FSC has been considered in this work because it has been reported to be a reproducible process and can refine the microstructure without producing unwanted textures, thereby reducing anisotropy (Catalini et al., 2013; Jiang et al., 2017; Komarasamy et al., 2021). It was also reported to produce favorable secondary precipitates such as dispersoids in ODS MA956 during friction consolidation (Catalini et al., 2013).

Figure 3. Schematic of recycling by FSC of alloy machining chips to produce alloy billets.

Three nuclear grade materials (Table 3) have been processed by FSC to evaluate the feasibility of this process for the efficient recovery of materials.

A709: Alloy 709 (Fe–20Cr–25Ni with other minor elements such as Mo, Mn, Nb, N, C, etc.) is a 20Cr–25Ni austenitic grade stainless steel and has been considered for sodium-cooled fast reactors (SFRs). Alloy 709 is a niobium-strengthened steel owing to the presence of nanoscale carbides (Upadhayay et al., 2018). It has a greater creep strength and better swelling resistance under self-ion irradiation than stainless steel 316 (Kim et al. 2019) and Grade 91 (Smith et al. 2017). Thermal properties such as the thermal conductivity and specific heat capacity of Alloy 709 have been found to be well within the values reported for other high Cr and high Ni austenitic steels (Smith et al., 2017).

316H: Alloy 316H is a high carbon modification of Alloy 316 developed for use at elevated temperatures. The alloy is used for structural and pressure vessel applications at temperatures above 500°C (Mehmanparast et al., 2014). The higher carbon content of 316H imparts higher tensile and yield strengths than those of 316/316L. The corrosion resistance of Alloy 316H has been observed to be comparable to Alloy 316/316L.

IN617: Alloy 617 is a nickel–chromium–cobalt alloy that has many outstanding properties such as high-temperature oxidation resistance and corrosion resistance in various corrosive aqueous environments (Mankins et al., 1974). It is the sixth material cleared by the Boiler and Pressure Vessel Code (BPVC) for use in high-temperature nuclear reactors.

Table 3. Chemical compositions of the alloys used in friction consolidation. All numbers are in units of weight percent. "Bal" indicates "balance."

	с	AI	Cr	Co	Ni	Mn	Мо	N	Si	Р	s	Ti	Nb	в	Fe
Alloy 709	0.066		19.93		24.98	0.91	1.51	0.148	0.44	0.014	0.001	0.04	0.26	0.0045	Bal
316H	0.04–0.1		16–18		10–14	2.00	2–3		0.75	0.045	0.03				Bal.
IN617		0.8–1.5	20–24	10-15	Bal.	1	8–10		1		0.015			0.006	3

2.1 FSC Process

2.1.1 Chips Fabricated by Machining Metal Bars

The chips used in the subsequent friction consolidation experiments were produced using a milling machine, as illustrated in Figure 4. Metal bars (A709 steel, 316H steel, and Inconel 617 nickel alloy) were clamped and machined into metal chips. To prevent excessive oxidation during the milling process, continuous coolant was used to cool the milling drill. The metal chips were then dried before the friction consolidation experiments. Although the milling process parameters (rotation rate and traverse speed) can affect the morphology and size of the metal chips, this aspect is not considered in the current investigation.

2.1.2 Friction Consolidation Setup

The friction consolidation experiments were performed using the friction stir welding (FSW) machine at PNNL, depicted in Figure 5. Two tooling setups, MP159 and W–Re, were utilized. Initial experiments with A709 steel chips indicated that the consolidated material tends to adhere to the MP159 tool. Consequently, the W–Re tooling setup was employed for the subsequent experiments. There are three critical process variables during friction consolidation experiments: the loading force, rotation rate, and processing time. Additionally, the tool/chip interface can be monitored during friction consolidation. It is important to note that the temperature is influenced by the combination of the loading force and rotation rate. In the following section, all critical process variables, including the temperature, are provided. Three metals were selected for the current study: A709 steel, 316H stainless steel, and Inconel 617 nickel alloy. These metals were machined into chips for the friction consolidation experiments.

Figure 5. Friction consolidation setup. Left: MP159 tooling setup; right: W–Re tooling setup. The machine used for this study is the FSW machine (as shown in the right bottom).

2.2 Characterization Techniques

Optical microscopy: Optical images were acquired with a DSX-1000 Olympus Digital Microscope using a $3 \times$ lens with bright- and dark-field filters.

Microhardness: A Clark Instrument Series CM-802 Micro Indentation hardness tester was used at 300 gf for 10 s per indent.

Scanning electron microscopy (SEM): A JEOL 7600 and ThermoFisher Scientific Apreo 2 scanning electron microscope was used to collect SEM micrographs of the samples using both secondary (SE) and backscattered (BSE) electron modes. Elemental maps using energy dispersive spectroscopy (EDS) were also collected. The samples were further characterized using electron backscatter diffraction (EBSD) using the same instrument.

2.3 FSC of Fe-Based Alloys

In this study, two stainless steels—namely, A709 and 316H—have been studied to ascertain the feasibility of FSC for Fe-based alloys.

2.3.1 FSC of Alloy 709

Five experimental runs of friction consolidation for A709 steel chips were conducted, with the critical parameters listed in Table 4. For Run #1, the tooling was made of MP159, but the consolidated materials stuck to the tool, leading to switch the tool material to W–Re to reduce sticking and overheating. During Run #2, no material stuck to the tool, but the processing time was too short (~2 min) to consolidate the chips effectively. Consequently, the processing time was increased for Runs #3, #4, and #5. More importantly, it became evident that the loading force played a significant role in consolidating the materials. As the loading force increased from 2–4 kN in Run #3 to 10 kN in Run #4 and 20 kN in Run #5, the rotation rates were reduced from 300–350 RPM in Run #3 to 150 RPM in Run #4 and 100 RPM in Run #5 to maintain a consistent tool/chip interface temperature of 850°C.

The cross-sectional images in Figure 6 show an increase in fully consolidated layer thickness from Run #3 to Runs #4 and #5. Hence, it can be reasonably inferred that the loading force has

a more significant impact on the consolidation level compared to the processing time. Additionally, machine data, including the tool position (Z position), loading force (Z-axis force), tool/chip interface temperature, rotation rate, and spindle torque for these five runs, are plotted in Figure 7.

					T	Duccesium
Run #	Weld #	Tool	Loading (kN)	Rotation rate (RPM)	remperature (°C)	time (s)
1	2023-10-28-#004	MP159	4–8	500	More than 1000	40
2	2023-10-28-#005	W-Re	2–4	150–200	Up to 450	120
3	2023-10-28-#006	W-Re	2–4	300–350	Up to 850	830
4	2024-04-11-#002	W-Re	10	150	Up to 850	650
5	2024-04-12-#000	W-Re	20	100	Up to 850	320

 Table 4.
 Critical parameters for friction consolidation of A709 steel chips.

Figure 6. Top row: Top views of the consolidated chips for Runs #3, #4, and #5 (A709 steel). Bottom row: Optical images of the cross sections.

Figure 8(a–b) show an SEM image and EBSD map of the as-received sample of A709, respectively. The grains of the as-received A709 sample can be observed with significant size variations. Figure 8(a) shows some precipitates in this alloy. The grain size was quantified and is listed in Table 5.

Figure 7. Machine data of the tool position (Z position), loading force (Z-axis force), tool/chip interface temperature, rotation rate, and spindle torque for Alloy 709 for Runs #1–#5.

Figure 8. (a) SEM image and (b) EBSD map showing the grain structure in the as-cast A709 sample.

Figure 9(a) shows the EBSD orientation map that reveals the grain structure of the FSC A709 sample. The grains appear to be equiaxed and refined, and the grain sizes for each run are presented in Table 5. As summarized in Table 5, the average grain size of the as-received A709 sample is nominally 10 μ m, while it is nominally 2 μ m for the friction-consolidated samples. The range of grain sizes is also at the higher end for the as-received sample compared to the friction-consolidated samples. Microhardness data collected for the as-received and FSC

samples are shown in Figure 9(b) and summarized in Table 5. The hardness of the frictionconsolidated sample varies from 246 to 287 HV, with variations corresponding to the locations of indentation in the sample. The as-received sample had an average hardness value of 194 ± 3 HV with hardness values in the range of 186–201 HV. This higher hardness of the frictionconsolidated samples can primarily be due to the smaller grain size of the friction-consolidated samples, in agreement with the Hall–Petch relationship (Hall 1951).

Figure 9. (a) EBSD map of FSC A709 showing the finer and equiaxed grain structure and (b) hardness plot of the as-received and FSC A709 samples.

Sample	Grain Size (µm)	Standard Deviation (µm)	Hardness (HV)	Standard Deviation (HV)
As-received	10.2	6.8	194.3	3.3
Run #1	3.6	0.9	287.3	12.9
Run #2	1.58	1.1	246.6	28.2
Run #3	1.95	1.0	260.2	16.2

Table 5.	Grain size ar	d microhardness	values of	as-received	and FSC	A709 samp	oles.
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An optical microscopy image of the cross section of a friction-consolidated A709 sample (Run #5) is shown in Figure 10(a). From this image, the middle part of the consolidated product shows no significant pores or defects. A709 chip consolidation is observed to be lower towards both ends. Figure 10(b) shows a montage of SEM images collected from the dense consolidated part enclosed by the black box in Figure 10(a). This area was analyzed by SEM, and images at different magnifications were collected. The grains from all areas appear to be equiaxed and finer compared to those in as-received A709 sample. Further, grain boundary precipitates are retained in the FSC product.

Figure 10. (a) Optical image of an FSC A709 sample. The black rectangular in (a) indicates the location of the SEM images in (b).

2.3.2 FSC of Alloy 316H

Three runs of friction consolidation for 316H steel chips were conducted, with the critical parameters listed in Table 6. As the loading force increased from 20 kN in Run #1 to 30 kN in Run #2, the rotation rates were reduced from 100–110 RPM in Run #1 to 70–100 RPM in Run #2 to maintain a consistent tool/chip interface temperature of 850°C. For Run #3, a low rotation rate range was selected to reduce the tool/chip interface temperature and test the viability of the low-temperature friction consolidation concept. The proposed mechanism implies that "harder" chips could transfer the load to the bottom chips more effectively. However, the results indicate that low-temperature friction consolidation negatively impacts the compaction level, as evidenced by the outcomes of Run #3.

Run #	Weld #	ΤοοΙ	Loading (kN)	Rotation rate (RPM)	Temperature (°C)	Processing time (s)
1	2024-05-08-#000	W–Re	20	100–110	Up to 850	420
2	2024-05-08-#001	W–Re	30	70–100	Up to 850	420
3	2024-05-08-#002	W–Re	30	35–50	Up to 650	420

Table 6. Critical parameters for the friction consolidation of 316H steel chips.

Figure 11. Top row: Side views of the consolidated chips for Runs #1, #2, and #3 (316 H steel). Bottom row: Optical images of the cross sections.

The side-view and cross-sectional images in Figure 11 show an increase in the fully consolidated layer thickness from Run #1 to Run #2. This suggests that the loading force has an evident impact on the consolidation level. Run #3 has the lowest compaction level compared with Runs #1 and #2. Additionally, machine data, including the tool position (Z position), loading force (Z-axis force), temperature, rotation rate, and spindle torque for these three runs, are plotted in Figure 12.

Figure 12. Machine data of the tool position (Z position), loading force (Z-axis force), tool/chip interface temperature, rotation rate, and spindle torque for Runs #1–#3.

An optical microscopy image of the cross section of a friction-consolidated 316H sample (Run #2) is shown in Figure 13(a). From this image, the top part of the middle region of the consolidated product shows no significant pore spacing or defects. However, the extent of consolidation appears to be lower compared to that in A709. The consolidation of 316H chips is observed to be even lower towards both ends. Figure 13(b) shows a montage of SEM images collected from the dense consolidated part indicated by the black line in Figure 13(a). This area was analyzed by SEM, and images at different magnifications were collected. Further, grain boundary precipitates are retained in the FSC product. The lack of consolidation towards the lower end of the samples is visible in the SEM images.

Figure 13. (a) Optical image of an FSC 316H sample. The black line in (a) indicates the location of the SEM images in (b).

Figure 14 shows EDS maps of a certain area of the FSC 316H sample (Run #2), where Si- and W-rich regions are observed. The 316H sample does not contain W, so the observed W can be from the W–Re tool used in this study. Figure 15(a) shows the EBSD orientation map that reveals the grain structure of the FSC 316H sample. The grains are equiaxed and refined, and the grain sizes for each run are listed in Table 7. Figure 15(b) shows a plot of the microhardness of the FSC 316H samples. The values of the hardness are provided in Table 7.

Figure 14. EDS map of the FSC 316H sample, showing the presence of W and Si.

Figure 15. (a) EBSD map of the FSC 316H sample, showing a finer and equiaxed grain structure and (b) hardness plot of the FSC 316H samples.

Sample	Grain Size (μm)	Standard Deviation (μm)	Hardness (HV)	Standard Deviation (HV)
Run #1	0.77	0.51	208.2	15.57
Run #2	0.55	0.27	227.78	12.02

Table 7. Grain sizes and microhardness values of the FSC 316H samples.

2.4 FSC of Ni-Based Alloys

Alloy 617 is a nickel–chromium–cobalt alloy and the sixth material cleared by the BPVC for use in high-temperature nuclear reactors.

2.4.1 FSC of Alloy 617

Four runs of friction consolidation for Inconel 617 nickel alloy chips were conducted, with the critical parameters listed in Table 8. As the loading force was increased from 20 kN in Run #1 to 35, 50, and 65 kN in Runs #2, #3, and #4, respectively, the rotation rates were reduced from 100–150 RPM in Run #1 to 50–100, 40–100, and 30–100 RPM in Runs #2, #3, and #4, respectively, to maintain a consistent tool/chip interface temperature of 900°C.

Run #	Weld #	Tool	Loading (kN)	Rotation rate (RPM)	Temperature (°C)	Processing time (s)
1	2024-04-30#000	W–Re	20	100–150	Up to 900	150
2	2024-04-30#001	W–Re	35	50–100	Up to 900	180
3	2024-05-03#000	W–Re	50	40–100	Up to 900	180
4	2024-05-03#001	W–Re	65	30–100	Up to 900	180

Table 8. Critical parameters for friction consolidation of Inconel 617 alloy chips.

The cross-sectional images in Figure 16 show an increase in the fully consolidated layer thickness from Run #1 to Runs #2, #3, and #4. Additionally, machine data, including the tool position (Z position), loading force (Z-axis force), temperature, rotation rate, spindle torque, and spindle power for these four runs, are plotted in Figure 17.

Figure 16. Top row: Top views of consolidated chips for Runs #1, #2, #3, and #4 (Inconel 617 nickel alloy). Bottom row: Optical images of the cross sections.

Figure 18(a–b) show an SEM image and EBSD map of the as-received sample of IN617, respectively. The grains of the as-received IN617 sample can be observed with significant size variations. The grain size was quantified is listed in Table 9.

Figure 17. Machine data of the tool position (Z position), loading force (Z-axis force), tool/chip interface temperature, rotation rate, and spindle torque for Runs #1–#4.

Figure 18. (a) SEM image and (b) EBSD map showing the grain structure of the as-received IN617 material.

An optical image of the cross section of a friction-consolidated IN617 sample (Run #4) is shown in Figure 19(a). From this image, the middle part of the consolidated product shows no significant pore spacing or defects. The consolidation of IN617 chips is observed to be lower towards both ends. Figure 19(b) shows a montage of SEM images collected from the dense consolidated part indicated by the black line in Figure 19(a). This area was analyzed by SEM, and images at different magnifications were collected. The grains from all areas appear to be equiaxed and finer compared to those in the as-received IN617 sample. Further, grain boundary precipitates are retained in the FSC product.

Figure 19. (a) Optical image of the FSC IN617 sample. The black line in (a) indicates the location of the SEM images in (b).

Figure 20(a) shows an EBSD orientation map that reveals the grain structure of the FSC IN617 sample. The grains appear to be equiaxed and refined, and the grain sizes for each run are

summarized in Table 9. Figure 20(b) shows a plot of the microhardness of the as-received and FSC IN617 samples. The values of the hardness are provided in Table 9. It is observed that the FSC samples have a higher hardness due to finer grains.

Figure 20. (a) EBSD map of an FSC A709 sample showing a finer and equiaxed grain structure and (b) a plot of the hardness of the as-received and FSC A709 samples.

Table 9.	Grain sizes and	microhardness	values of	as-received	and FSC IN	617 samples.
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Sample	Grain Size (µm)	Standard Deviation (µm)	Hardness (HV)	Standard Deviation (HV)
As-received	10.2	6.8	230.7	6.78
Run #3	1.35	0.67	356.49	13.75
Run #4	1.14	0.88	361.38	22.89

2.5 FSC Discussion

Evolution of the relative density during friction consolidation: According to the machine data, the real-time relative density of the chips during the friction consolidation experiments can be measured.

This section presents the results of Inconel 617 friction consolidation experiments. As shown in Figure 21, there are four stages during friction consolidation:

- Stage 1: The relative density rapidly increases without a significant rise in temperature. This stage is very brief, lasting around 15 s.
- Stage 2: The increase in the relative density slows compared to that in Stage 1, while the tool/chip interface temperature begins to rise towards its peak.
- Stage 3: The relative density increases again, faster than that in Stage 2 but slower than that in Stage 1. During this stage, the tool/chip interface temperature stabilizes at its peak.
- Stage 4: The increase in the relative density slows but continues at a steady rate. The tool/chip interface temperature remains constant at its peak level.

Figure 21. Relative density vs. time (left) and tool/chip interface temperature vs. time (right) for Runs #1–#4 of the friction consolidation of Inconel 617 chips.

2.6 FSC Summary

This work aims to ascertain the feasibility of FSC as a materials recycling process utilizing three nuclear-reactor-relevant alloys. The main findings are summarized below:

- 1. In the FSC process, metal chips were successfully solid-state-consolidated into dense products after optimization of the process parameters. The extents of consolidation in the A709 and IN617 alloys were higher than that in the 316H alloy. Further, the real-time density evolution was measured, revealing the mechanism of the consolidation process.
- In all three alloys (A709, 316H, and IN617) that were FSC-processed, the grains were refined in size and were nearly equiaxed, removing any anisotropy from the starting material. In A709, the grain size decreased by nearly 80 percentage (from 10 to 2 μm). Similarly, the grain size reduction was nearly 88 percentage in IN617 (from 10.2 to 1.2 μm).
- 3. Subsequently, the hardness of the FSC product substantially increased owing to grain boundary strengthening (Hall–Petch relationship).
- 4. In the 316H consolidation, small W and Si rich particles were observed in the chemical analysis. The W is possibly due to wearing the tool used for the friction-stir compaction.

3.0 Liquid Waste: Metal Recovery through Aqueous Separation

3.1 Introduction

Increasing attention has been given to the recovery of CMs from industrial wastewater in the United States and globally. Figure 22 shows that certain untreated industrial wastewater contains high concentrations of CMs. For example, electroplating processes generate a maximum of over 80,000 mg/L of Ni in their wastewater (Gorokhovsky et al., 2020) and mining processes have 6,900–11,000 mg/L of Ni. Mining and tannery processes have high concentrations of Co (700–1,100 mg/L), Mn (23–200 mg/L), and Cr (140–2000 mg/L) (Capilitan et al., 2023; Mohammed and Yaacob 2016).

Figure 22. Concentrations of CMs from various untreated industrial wastewater.

Therefore, the recovery of CMs from industrial wastewater is beneficial for providing an alternative to primary resources, enhancing the recycling rate of minerals, and reducing potential hazards to environmental safety and human health (Thallapally et al., 2024). Various technologies have been explored to recover CMs from wastewater, including chemical precipitation, ion exchange, membrane filtration, adsorption, solvent extraction, and electrochemical treatment techniques (Qasem et al., 2021). Some of these processes have significant disadvantages such as incomplete removal, high energy requirements, and the production of toxic sludge. Adsorption has become one of the techniques most readily used owing to the simplicity of the process, cost-effectiveness, efficiency, the generation of low amount of sludge, and low reagent consumption. Most adsorbents including activated carbons (Kołodyńska et al., 2017), zeolites (Lu et al., 2016), and functionalized metal-organic frameworks (MOFs) (Peng et al., 2018) for the removal of heavy metals often require a time of 4-24 h in contact with brine to reach their adsorption equilibrium. For real-world applications in the mineral recovery industry, adsorbents need to exhibit a rapid mineral uptake combined with a high adsorption capacity and chemical stability. Moreover, powdered adsorbents have limited use in practical applications because they are difficult to handle and recover from liquids after mineral uptake. PNNL has patented a magnetic nanofluid extraction technology to extract rareearth elements from brines (Figure 23) (Elsaidi et al., 2018; Liu et al., 2024). In brief, core-shell composite nanoparticles will be produced that contain a magnetic iron oxide core (Fe₃O₄) surrounded by a shell made of an ionic metal-organic framework (iMOF) functionalized with chelating ligands selective for CMs. By introducing core-shell particles at a low concentration

into the brine, the brine is exposed to a very high concentration of chelating sites on the nanoparticles without the need to pass through a large and costly traditional packed bed or membrane system where the pressure drops, and parasitic pumping power losses are significant issues. Instead, after a short residence time flowing with the brine, the particles are effectively separated with an electromagnet, and standard extraction methods are then applied to strip the rare-earth metals from the nanoparticles, which are then recycled back to the geothermal plant. Preliminary estimates using this nanofluid-based method suggest recovery efficiencies can easily exceed 90%, and production costs for Nd, Dy, Y, and Eu are less than half the present commodity market values for these metals. Further, the same technology was extended to extract lithium from geothermal and produced waters as part of the DOE Advanced Manufacturing Office. This technology has been commercialized to Moselle Technologies who has exclusive license. The exact magnetic process may not be ideal for the current application, but the magnetic separation process can be tailored to extract nickel from AM scrap and other process, which PNNL might have unique intellectual property if demonstrated at the laboratory scale. Like the magnetic process, other approaches will also be explored such as electrochemical separation approaches to extract nickel from aqueous solution.

Figure 23. Schematic of the magnetic nanofluid extraction system (Elsaidi et al., 2018).

Therefore, our first step is to identify a sorbent that possesses a high adsorption capacity, chemical stability, and rapid mineral uptake for the extraction of CMs from aqueous solution. The proposed sorbents can be potentially engineered for electrochemical or magnetic separation to meet the demand of practical applicability and commercialization.

Figure 24. Schematic showing the impact of the electrochemical separation of CMs from aqueous sources on the full CM lifecycle.

3.2 Extraction of CMs

3.2.1 Synthesis of Anionic Frameworks as Adsorbents

A series of iMOFs were synthesized under solvothermal conditions (Svensson Grape et al., 2023) (Figure 25(a, b). Since it is an anionic framework, there are charge-balancing cations such as dimethylammonium (DMA) in the pores to stabilize the framework structure. The DMA ions in the pores of iMOF(DMA) can be easily exchanged with lithium (Li), sodium (Na), and potassium (K) ions, resulting in the formation of iMOF(Li), iMOF(Na), and iMOF(K), respectively.

Figure 25. (a) Crystal structure of an iMOF (Svensson Grape et al., 2023), (b) scanning electron microscope image of iMOF(DMA) crystals, (c) powder X-ray diffraction patterns, and (d) nitrogen adsorption–desorption isotherms of iMOFs.

The powder X-ray diffraction (PXRD) patterns of the iMOFs [Figure 25(c)] show identical diffraction peaks, confirming that the crystal structures of the iMOFs remain intact after cation exchange. It is noted that the nitrogen adsorption–desorption isotherms measured at 77 K [Figure 25(d)] illustrate that cation exchange leads to an increase in the Brunauer–Emmett–Teller (BET) surface areas of the iMOFs. Exchanging the charge-balancing cation from DMA to Li, Na, and K increases the surface area from 273.5 m²/g to 505.3, 388.4, and 390.1 m²/g, respectively. This could be due to the replacement of bulkier DMA ion with smaller ion. Elemental analyses of the iMOFs (Table 10) show that DMA ions were fully exchanged to Li, Na, and K ions.

	C (wt%)	N (wt%)	Zr (wt%)	Li (wt%)	Na (wt%)	K (wt%)
iMOF (DMA)	45.69	6.5	8.41	-	-	-
iMOF (Li)	37.35	0.58	10.26	1.54	-	-
iMOF (Na)	36.51	0.58	10.27	-	4.7	-
iMOF (K)	36.40	0.69	9.94	-	-	6.27

Table 10. Compositions of iMOFs.

3.2.2 pH Stability of iMOFs

Industrial wastewater, which is generated after electroplating, mining, tannery, and smelting processes, is complex and can have various pH ranges. Therefore, the stability of iMOFs under harsh chemical conditions is vital for industrial applications such as the treatment of wastewater sludge. The pH stability of iMOFs was evaluated by exposing iMOF(DMA to aqueous solutions of HCl or NaOH for more than 24 h. As shown in Figure 26, the structure of the iMOF remained unchanged under highly acidic (pH 1) and highly basic (pH 11) conditions, proving that the iMOF is highly stable in aqueous solution over a wide range of pH values. The results show that the iMOF is suitable for use in industrial wastewater.

Figure 26. PXRD patterns of the iMOF after being exposed to various pH levels in aqueous solution at room temperature.

3.2.3 Nickel Extraction from Aqueous Brine by iMOFs

A batch adsorption study of Ni was carried out by suspending an iMOF (3 mg/mL) in nickel(II) nitrate solutions (Ni concentration = 100 mg/L) at room temperature and measuring the Ni concentration in the supernatant solution using inductively coupled plasma optical emission spectroscopy (ICP-OES). To investigate the Ni uptake performance of the iMOF, the Ni adsorption capacity (Q) and Ni removal efficiency were respectively calculated using

$$Q = \frac{C_{\rm Ni,0} - C_{\rm Ni,e}}{C_{\rm iMOF}} \tag{1}$$

Ni removal efficiency (%) =
$$\frac{(C_{\text{Ni},0} - C_{\text{Ni},e})}{C_{\text{Ni},0}} \times 100$$
 (2)

where

Q = the Ni adsorption capacity (mg/g)

 $C_{Ni,0}$ = the initial concentration of Ni in the solution (mg/L)

 $C_{\text{Ni,e}}$ = the equilibrium concentration of Ni in the solution (mg/L)

 C_{iMOF} = the concentration of the iMOF in the solution (mg/L).

The Ni adsorption capacities are 33.4 mg/g for iMOF(DMA) and 34.1 mg/g for iMOF(Li), iMOF(Na), and iMOF(K) [Figure 27(a)]. As shown in Figure 27(b), the Ni removal efficiency of iMOF(DMA) is 97.8%. iMOF(Li), iMOF(Na), and iMOF(K) perform perfectly to extract Ni, and the removal efficiencies are >99.9%. The Ni adsorption kinetics of iMOF was further studied at 4 mg/mL of iMOF in brine (Ni concentration = 100 mg/L). Ni was completely removed by iMOF(Li), iMOF(Na), and iMOF(K) within a soaking time of 5 min (>99.9% removal efficiency) [Figure 27(b)]. Compared to other previously reported MOF-based adsorbents (Piątek et al., 2021), which require 24 h of contact time to reach their adsorption equilibrium, the adsorption of Ni by the iMOF is a rapid and efficient process that is essential for the industrial Ni recovery process.

Figure 27. (a) Ni adsorption capacities and (b) Ni removal efficiencies of iMOFs.

To investigate the mechanism behind the Ni adsorption by an iMOF, the adsorption kinetics data were modeled with the following pseudo-second-order kinetics equation (Ünlü and Ersoz 2007):

$$\frac{t}{Q_{\rm t}} = \frac{1}{kQ_{\rm e}^2} + \frac{t}{Q_{\rm e}} \tag{3}$$

where

- Q_t = the Ni adsorption capacity at time t (mg/g)
- Q_e = the Ni adsorption capacity at equilibrium (mg/g)
 - t = the adsorption time (min)
- k = the adsorption rate constant [g/(mg·min)].

Table 1 [°]	1. Kinetic	parameters of N	li adsorption	using a	pseudo-second-	order kinetic model.
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	R^2	<i>k</i> (g/mg∙min)	Q _{e,model} (mg/g)	Q _{e,exp} (mg/g)
iMOF(DMA)	0.999	0.212	25.71	25.50
iMOF(Li)	0.999	0.332	25.84	25.60
iMOF(Na)	0.999	0.266	25.90	25.60
iMOF(K)	0.999	0.286	25.90	25.60

Table 11 summarizes the model parameters and correlation coefficients (R^2) obtained from a linear fitting of the results in Figure 27(b). The R^2 values for the pseudo-second-order kinetics model are above 0.999, and the Q_e values calculated by the model ($Q_{e,model}$) are very close to the experimental values ($Q_{e,exp}$). The results show that the pseudo-second-order kinetics model

is suitable for describing the Ni adsorption onto the iMOF and that the adsorption process is chemisorption (ion exchange between Ni and the charge-balancing cation).

To investigate how much the charge-balancing cations in the pores of the iMOF are exchanged during Ni adsorption, the percentage of cation exchange was calculated as follows:

Cation exchange (%) =
$$\frac{C_{\text{cation}}}{C_{\text{iMOF}} \times \omega_{\text{cation}}} \times 100$$
 (4)

Where C_{cation} =the concentration of the cation in the solution (mg/L) C_{IMOF} $\overleftarrow{\omega}_{\text{cation}}$ $\overleftarrow{\omega}_{\text{cation}}$ $\overleftarrow{\omega}_{\text{cation}}$ ω_{cation} $\overleftarrow{\omega}_{\text{cation}}$ $\overleftarrow{\omega}_{\text{cation}}$ $\overleftarrow{\omega}_{\text{cation}}$

Figure 28(a) shows that 40%–45% of the cations (Li, Na, K) existing in the pores were exchanged during the Ni adsorption process.

Notably, the Ni-loaded iMOF can be regenerated by being washed in a high-concentration acid or salt solution [Figure 28(b)]. After the Ni-loaded iMOF(DMA) was immersed in a 1 M hydrochloric acid (HCl) solution for 1 h, the Ni concentration in the HCl solution increased to 59.4 ppm. Immersion in a 1 M dimethylammonium chloride (DMACl) solution led to Ni release from the Ni-loaded iMOF(DMA) as well, and the Ni concentration in the DMACl solution increased to 38.6 ppm. The results indicate that the extracted Ni can be collected and concentrated in an acid or salt solution.

3.2.4 Coextraction of CMs from Aqueous Brine by iMOFs

Considering that some aqueous brines may contain multiple minerals, batch adsorption was investigated by suspending an iMOF (4 mg/mL) in a brine containing five minerals (Table 12) at room temperature.

Ni (mg/L)	Mn (mg/L)	Cu (mg/L)	Fe (mg/L)	Co (mg/L)
100	100	100	100	100

Table 12. Composition of brine with multiple minerals.

The adsorption capacities and removal efficiencies for Ni, Mn, copper (Cu), iron (Fe), and Co shown in Figure 29(a, b) prove the effectiveness of the iMOF as a general adsorbent to extract multiple minerals simultaneously. Compared to the Ni adsorption capacity ($25.58 \pm 0.04 \text{ mg/g}$) and Ni removal efficiency ($99.5\% \pm 0.69\%$) of the iMOF in a brine containing Ni only (Figure 26), the Ni adsorption capacity and Ni removal efficiency of the iMOF were reduced to $13.19 \pm 0.52 \text{ mg/g}$ and $48.39\% \pm 0.48\%$, respectively, in a brine containing multiple metal ions. This is attributed to competition with coexisting minerals.

Figure 29. (a) Adsorption capacities, (b) removal efficiencies, and (c) selectivities of an iMOF in an aqueous brine containing multiple minerals.

The adsorption performance of the iMOF for multiple minerals was further analyzed in terms of the distribution coefficient (K_d) and selectivity (α), expressed as

$$K_{\rm d} = \frac{C_{\rm M,0} - C_{\rm M,e}}{C_{\rm M,e} \times C_{\rm iMOF}}$$
(5)

$$\alpha = \frac{K_{\rm d}^{\rm Ni}}{K_{\rm d}^{\rm M}} \tag{6}$$

where	$C_{M,0}$ = the initial concentration of the mineral in the solution (mg/L)
$C_{\rm M.e}$	Example 2 is the equilibrium concentration of the mineral in the solution (mg/L)

A larger K_d indicates more adsorption of the cation in the iMOF; therefore, a larger α indicates preferable adsorption of Ni over the coexisting mineral (M) in the brine. As shown in Figure 29(c), the α values for Ni/Mn (K_d^{Ni}/K_d^{Mn}) and Ni/Co (K_d^{Ni}/K_d^{Co}) are greater than 1, suggesting that the iMOF preferably adsorbs Ni compared to Mn and Co, whereas the α values for Ni/Cu (K_d^{Ni}/K_d^{Cu}) and Ni/Fe (K_d^{Ni}/K_d^{Fe}) are less than 1, suggesting that the iMOF preferably adsorbs Cu and Fe compared to Ni.

3.3 Ni Recovery: Conclusion and Next Steps

In conclusion, PNNL developed ionic framework-based adsorbents (iMOFs) for the recovery of CMs from aqueous brine. The synthesized adsorbents are highly stable in aqueous solution over wide pH ranges and show excellent mineral removal efficiency (>99.9%) within 5 min, indicating efficient mineral extraction capability from industrial wastewater. Based on current research work, future work is needed to investigate the cycling performance of the iMOFs and the controlled release of multiple minerals captured by an iMOF simultaneously. Despite the major advantages of the developed iMOFs encompassing chemical stability, a high adsorption capacity, and rapid mineral uptake, their major limitation is their processability in powder form, which limits their applicability in real-world applications. Hence, extensive research efforts need to be devoted to the construction of more robust and portable forms such as engineered particles, thin films, or membranes combined with electrochemical and/or magnetic separation to meet the demands of practical applicability and commercialization.

4.0 Conclusions and Next Steps

In this report, experimental feasibility studies showed the positive impacts of the recycling of solid waste through the consolidation of machining chips or offcuts and liquid waste metal recovery through aqueous separation for nuclear material supply risks.

The solid-state recovery or recycling of CMs involves the use of alloy shavings or machined chips as the starting materials for FSC to produce dense billets that can be extruded to different useful dimensions. This process shows the benefit of a full circular process, with no waste of CMs, and can be repeated several times. FSC has been considered in this work because it has been reported to be a reproducible process and can refine the microstructure without producing unwanted textures, thereby reducing anisotropy.

Three nuclear grade materials have been processed by FSC to evaluate the feasibility of this process for the efficient recovery of materials: (1) Alloy 709 (Fe–20Cr–25Ni with other minor elements such as Mo, Mn, Nb, N, C, etc.) is a 20Cr–25Ni austenitic grade stainless steel and has been considered for SFRs. (2) Alloy 316H is a high carbon modification of Alloy 316 developed for use at elevated temperatures. The alloy is used for structural and pressure vessel applications at temperatures above 500°C and is currently considered for multiple reactor types. (3) Alloy 617 is a nickel–chromium–cobalt alloy that has many outstanding properties such as high-temperature oxidation resistance and corrosion resistance in various corrosive aqueous environments. It is the sixth material cleared by the BPVC for use in high-temperature nuclear reactors.

In the FSC process, metal chips of all three alloys were successfully solid-state-consolidated into dense products after limited optimization of the process parameters. The extents of consolidation in A709 and IN617 are higher compared to that in 316H. Further, the real-time density evolution was measured, revealing the mechanism of the consolidation process, which will allow for future upscaling benefits. In all three alloys (A709, 316H, and IN617) that were FSC-processed, the grains are refined in size and nearly equiaxed, removing any anisotropy from the starting material. In A709, the grain size decreased by nearly 80 percentage (from 10 to 2 μ m). Similarly, the grain size reduction was nearly 88 percentage in IN617 (from 10.2 to 1.2 μ m). Subsequently, the hardness of the FSC product substantially increases owing to grain boundary strengthening (Hall–Petch Relationship).

The development of simple and cost-effective techniques for CM production and recovery from industrial wastewater will enhance the current recycling rate of minerals and reduce the potential hazards of industrial wastewater bearing high concentrations of minerals. In this project, iMOF-based adsorbents were successfully designed for CM extraction from aqueous solution. These sorbents can be integrated into electrochemical or magnetic separation approaches to meet the demands of practical applicability and commercialization. The synthesized iMOFs were characterized using various techniques to understand their physicochemical properties. The iMOFs encompass chemical stability, a high adsorption capacity, and rapid mineral uptake. Specifically, the iMOFs are highly stable in aqueous solution over wide pH ranges, indicating that they are suitable for use in industrial wastewater with harsh chemical environments. The uptake properties of the iMOFs were evaluated in terms of the adsorption capacity, removal efficiency, and kinetics. The adsorption capacity of iMOFs towards nickel reaches 34.1 mg/g with a removal efficiency of >99.9%. Notably, nickel is completely removed within 5 min, which is much faster compared to other adsorbents. Moreover, the iMOFs can simultaneously coextract multiple minerals, proving their effectiveness as general adsorbents

A simple and compact system can achieve recovery and recycling efficiencies of over 90%, which will push peak mineral production and delay the scarcity of alloying minerals by exposing the industrial water solution to a selective sorbent. The improvements in CM recovery will accelerate the electrification of the transportation sector, provide a new source of CMs for stainless-steel manufacturing processes, and position the United States ahead of its competitors in the sustainable economy development. The next steps are to extend the sorbent technology for CMs with a high selectivity and capacity to accommodate a much higher throughput.

In summary, this project provides evidence of the successful recycling of solid waste offcuts resulting from conventional manufacturing processes from three relevant alloys to next-generation nuclear reactor developers, potentially providing upscaling for a circular process, where no critical element will be lost. Furthermore, iMOF-based adsorbents were successfully designed for CM extraction from aqueous solution, thereby providing a pathway for future upscaling opportunities for salvaging dissolved Ni ions. This research has achieved its goal of showing the impact of novel applications of recycling technologies for solid and liquid waste that can be upscaled for application.

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