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Desorption and Migration Behavior of Beryllium from Contaminated Soils: Insights for Risk-Based Management

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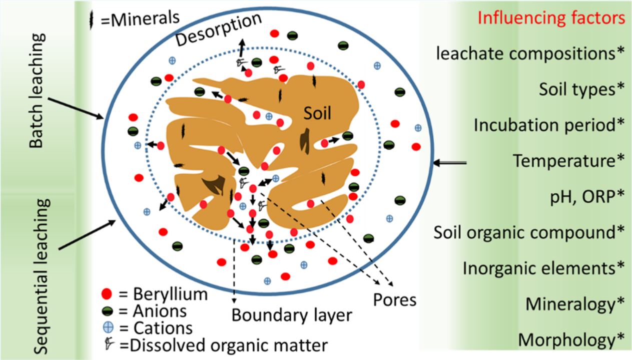
ABSTRACT: Factors influencing the desorption, distribution, and vertical migration behavior of Be in contaminated soils are not fully understood. This study examined the desorption and migration of Be in a soil profile from a legacy radioactive waste disposal site using different batch leaching [monofilled waste extraction procedure (MWEP); synthetic precipitation leaching procedure (SPLP); simulated acid rain solution (SARS); and toxicity characteristic leaching procedure] and sequential leaching [community bureau of reference (BCR)] methods for insights relevant to the application of risk-based management. The results showed that Be desorption was higher in the presence of organic than the inorganic leachate composition (MWEP < SPLP < SARS < TCLP < BCR first-step). The desorption followed three diffusion control mechanisms, which resulted in three desorption rate constant estimates of 157, 87.1, and 40.4 Be/kg.h$^{0.5}$, and the estimated desorption maximum was 556 μg/kg. The desorption process was, spontaneous ($\Delta G > 0$), enthalpically and entropically influenced. Increasing the incubation period and heat treatment resulted in a decrease of Be desorption and migration. The soil clay content and pH were the primary factors influencing Be desorption, and the results suggested that Be was desorbed from metal oxyhydroxides and surfaces of silicates (e.g., reactive surfaces of clay minerals), organic matters, and soil pores. Because of high K_d values, the mobility of Be was limited, and no exceedances of ecological or human health risk index or guidelines were determined for the current contamination levels at the site. However, Be released from the waste trenches has the ongoing potential to increase Be concentration in the soil.



1. INTRODUCTION

Beryllium (Be) waste in the surface or subsurface soil may be a threat to the environment and ecosystem's health when desorbed and mobilized, presenting a challenge for the management of contaminated sites. Beryllium is highly reactive in the environment, hydrates readily and is toxic to plants and animals even at very low (<0.004 mg/L) concentrations.[1−3] In addition, it is categorized as a class one human carcinogen.[4] A specific concern is the widespread use of Be for many scientific and technological applications, including defence, aerospace, automotive, nuclear energy, medical, electronic industries, and so forth.[5,6] Subsequently, it may be released to the environment during manufacturing, handling, and waste disposal. Furthermore, 20 tons of Be/year were emitted to the atmosphere from Europe[7] and ∼4.5 tons/year from Australia,[8] which represents a potential risk after wet and dry deposition for mobilization from soil and arising from surface or groundwater acidification.[9−11] However, some researchers have suggested that Be has low mobility under oxidizing and acidic conditions.[11,12] Other researchers[13,14] have reported that the mobility of Be primarily depends on pH, but the presence of different soluble metals, nonmetals, and minerals is also influential on the Be chemistry. Therefore, the desorption and migration behavior of Be in the environment are not yet well understood.

To evaluate the environmental mobility and associated risk of metals, different batch and sequential leaching tests have long been utilized.[15−17] Batch leaching of metals has many advantages (simple, low cost, ability to control pH, etc.) over column leaching,[18] and different batch leaching techniques [e.g., monofilled waste extraction procedure (MWEP), synthetic precipitation leaching procedure (SPLP), and toxicity characteristic leaching procedure (TCLP)] are well established for different heavy metal desorption, migration, and toxicity assessment.[16,19] Different factors affect the batch leaching of metals,[18] including pH, soil type, time, temperature, and the presence of soluble metals or nonmetals. Different batch leaching methods and the potential immobilization of Be from

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the industrial solid waste derived from bauxite processing (red-mud) have been reported in the literature,[2,20] but the data are still limited for Be-contaminated soils.

The MWEP and SPLP (which simulates acid rain) are standard tests, which have been recommended for metal (loid) leaching/desorption, and represent the potential for ground or surface water contamination.[16,21] However, rainwater chemical compositions vary regionally; therefore, compositions reflecting local rainwater are most relevant.

Leaching protocols simulate conditions where water might pass through waste, with metals being classified as readily bioavailable, potentially bioavailable, or not bioavailable.[22] Therefore, it is important to speciate the total amount of contaminants into different bioavailable and non-bioavailable fractions, and this aspect has been demonstrated by different sequential leaching protocols.[17,23] In the BCR (community bureau of reference) sequential leaching procedure, the leaching metal in the first step (F1) is readily bioavailable; the second (F2) and third (F3) fractions are potentially bioavailable, whereas the consolidated fourth fraction (F4) is not bioavailable.[23,24]

The objective of this study is to explore the desorption and migration or transport behavior of Be from the contaminated soil of a legacy radioactive waste disposal site in Sydney, Australia, where a significant amount of Be (~1070 kg) was disposed. The site is representative of similar international sites.[13] The applied methods include several batch leaching, simulated acid rain representing the local conditions, and sequential leaching methods. The results of this work will help guide the application of risk-based management for the site. Different factors, including leachate compositions, soil types, time, temperature, electrochemical properties, soil organic–inorganic elements, mineralogy, and morphology, were evaluated for explaining the mechanism of desorption and migration of Be, and this information is essential for the potential management of Be contamination.

2. RESULTS AND DISCUSSION

2.1. Desorption of Be Using Different Batch Leaching.

The amounts of Be desorbed was significantly different ($P < 0.05$) using different batch leaching methods (Figure 1). Beryllium desorption using the inorganic leachates simulated acid rain solution (SARS), MWEP, and SPLP was in the range of 122–142 μg/kg (mean 128 μg/kg), 25.3–33.7 (31.1) μg/kg, and 53.3–63.4 (58.5) μg/kg, respectively (Table 1). The Be in the SARS extraction was 4.2 and 2.2 times higher than those of the MWEP and SPLP, respectively, and similar trends were also found for both the trenches and background soil, as well as in the spiked and unspiked (natural) soils (details in Table S1). Similar results among trench and background soils for each category of batch leaching might be due to the similar physicochemical properties of the Little Forest Legacy Site (LFLS) soil as reported earlier[13] (also see Table S2). The higher desorption in the SARS could be attributed to the effect of pH (pH 4.5), relatively higher buffering capacity, and presence of competing ions (Na^+, Mg^{2+} Ca^{2+}, K^+, and NH_4^+) and counter ions (e.g., Cl^-).

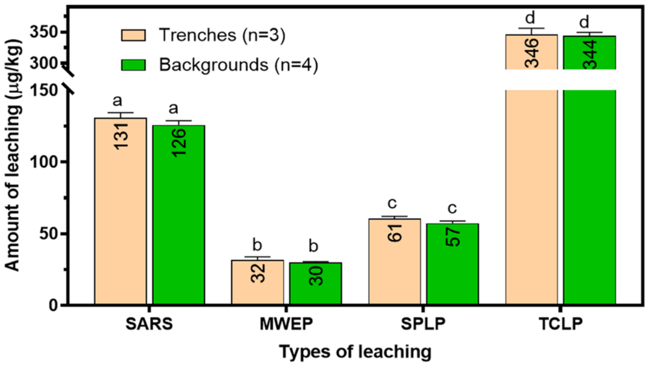

Figure 1. Desorption of Be using different batch leaching methods. Desorption of Be from LFLS soil under regional SARS, which was compared with different standard batch leaching procedures. Dissimilar letters represent a statistically significant ($P < 0.05$) difference among the variables.

Table 1. Desorption of Be from LFLS Soils (Mean ± SD) Using Different Batch Leaching Methods for Spiked and Natural Soils[a]

leaching protocol	*soil	leaching (μg/L)	L_r (%)	K_d (L/kg)
SARS	spiked (range)	6.09–7.08	2.07–2.76	724–966
	spiked (mean)	6.40 ± 0.08	2.37	848
	natural soil	0.070 ± 0.02	0.250	7990
MWEP	spiked (range)	1.27–1.70	0.426–0.661	3040–4660
	spiked (mean)	1.55 ± 0.06	0.575	3448
	natural soil	0.004 ± 0.001	0.080	139250
SPLP	spiked (range)	2.85–3.17	0.90–1.23	1626–2220
	spiked (mean)	2.93 ± 2.2	1.09	1834
	natural soil	0.05 ± 0.009	0.18	11088
TCLP	spiked (range)	16.0–19.4	5.55–6.83	292–360
	spiked (mean)	17.5 ± 0.51	6.37	314
	natural soil	0.101 ± 0.01	0.355	5635

[a] MWEP = monofilled solid waste extraction procedure; SARS = simulated acid rain solution; SPLP = synthetically precipitation leaching procedure; TCLP = toxicity characteristic leaching procedure; L_r = leaching ratio (leachable Be to total Be); * details of the data of Be desorption from spiked soils, see the Supporting Information.

Chloride ions form less stable complexes with Be (only ion-pair formation) than the other anions, including fluoride, phosphate, and carbonate,[25,26] resulting in enhancing the mobility of Be, and Naidu et al.[27] also reported a similar effect for cadmium (Cd) (both are divalent cations). In addition, excess hydrogen ions (H^+) in the acid rain compete with the target metal ions (i.e., Be) present in the binding sites of clay materials, oxyhydroxides of metals [aluminum (Al)/iron (Fe)/manganese (Mn)], and the lattice of secondary minerals such as carbonates, sulfates, oxides, and silicates, which influence metal mobility.[9,21,28]

Relatively lower K_d was found (indicating lower retardation or higher migration behavior) under SARS (mean 848 L/kg for spiked and 7990 L/kg for natural soils) than the SPLP (1834 and 11088 L/kg) and MWEP (3448 and 139250 L/kg). These data (Table 1) indicate the limited mobility or transport of Be from the natural soils (K_d = 7990–139,250 L/kg) but also the potential for mobilization of Be in soils when subjected to acid rain (pH < 4.5). The above leaching protocols represent the risk of groundwater or surface water contamination due to leaching of Be from the soil.[2,29] Townsend et al.[18] reported the application of SPLP to identify the potential for groundwater contamination, and this leachate concentration is generally compared to the drinking water standard, though the drinking water standard for Be varies from country to country (e.g., Australia 60 μg/L, USA 4 μg/L).[18,30,31] However, approximately 0.004−30 μg Be/L was reported previously in typical groundwater at the LFLS site,[32] which does not exceed the leachate concentration of Be from surface soil (0−10 cm depth) using MWEP, SPLP, and SARS for both natural and spiked soils. Surface soils contain relatively more Be and the presence of more geochemically reactive elements than subsurface soil (>15 cm),[11] which may explain why limited mobility of Be was reported under different leaching methods in this study using surface soil (further discussion of the potential risk is presented in Section 2.4).

Relatively higher desorption (mean 6.37% for spiked and 0.355% for natural soil) and lower K_d (314 and 5635 L/kg) of Be was measured in the TCLP (pH 4.93) leachate compared to the SARS (pH 4.5) (Table 1). This is attributed to the solubilization of Be in the presence of organic ligands, which have a greater complexation ability than the inorganic ligands. Loganathan et al.[33] reported greater Cd solubility (both Cd^{2+} and Be^{2+} are divalent cations) in the presence of organic ligands than many other inorganic ligands, which is also consistent with our results for Be solubility. Lower stability constant of acetic acid ($\log k = 1.6$) favor the formation of less stable complexes with Be[34] that could be solubilized because organic acid can dissolve insoluble metal by three mechanisms, namely, acidification, chelation (soluble complex), and exchange mechanisms.[35] Beryllium, in this case, possesses a very small size-to-charge ratio, hydrates readily, and forms complexes with the organic functional groups,[25,36] which are susceptible to be solubilized.[34,37] According to the USEPA guideline, any waste disposal site can be considered hazardous if the target metal (e.g., Be) concentration in the TCLP leachate exceeds 100 times the drinking water standard [e.g., Be (USA) = 4 × 100 = 400 μg/L] for that metal.[18] This amount was not exceeded in this study for Be, representing limited toxicity (details in Section 2.4).

Although it is clear from Figure 1 that the different leaching chemicals result in different degrees of extractability of Be from the soils, it is also worth commenting on the absence of significant differences between the trench soils and the background soils. This arises from two key factors. First, the trench soils have similar physicochemical properties to the background soils,[13] which reflects their source from trench excavation and additional fill material derived from local soils.[38] This leads to similar leaching behavior between trench and background soils. Second, the amount of Be added due to leaching from the trenches into the above-trench soils is clearly comparatively small.

2.2. Kinetics and Thermodynamics of Be Leaching.

In the batch kinetic leaching experiments of Be using SARS, the rate of desorption was very fast up to 1 h, and then, slow desorption was found to reach an equilibrium, characterized by three discontinuous lines (Figure S1). The amount of desorption and K_d did not change significantly ($p > 0.05$) after 1 h (Figure 2A).

However, considering the entire period (72 h), some regression relationships (R^2) of Be desorption were found with the solubility of different organic and inorganic elements. Specifically, dissolved organic carbon (DOC), EC, Mn, Barium (Ba), Strontium (Sr), and Zinc (Zn) showed a very strong regression relationship (R^2 = 0.827−0.987), and a moderate relationship (R^2 = 0.470−0.601) was also found in Cd, cobalt (Co), molybdenum (Mo), selenium (Se), and phosphorous (P) solubility (Figure S2 and Table S3). Different physicochemical factors influencing the distribution and desorption of Be were reported previously.[13,39,40] Edmunds[7] and Islam et al.[13] reported that soil organic matters and oxyhydroxide of metals are important factors controlling Be distribution and transport. Moreover, Pawlowski and Karwan[41] reported that the mobility of Be increased with the increase in DOC, and Taylor et al.[42] reported that Be-humate/fulvate complexes are often unstable and can be mobile in the environment, which may also be applied in this study, resulted in strong correlation (R^2 = 0.926) between DOC and amount of Be in the leachate.

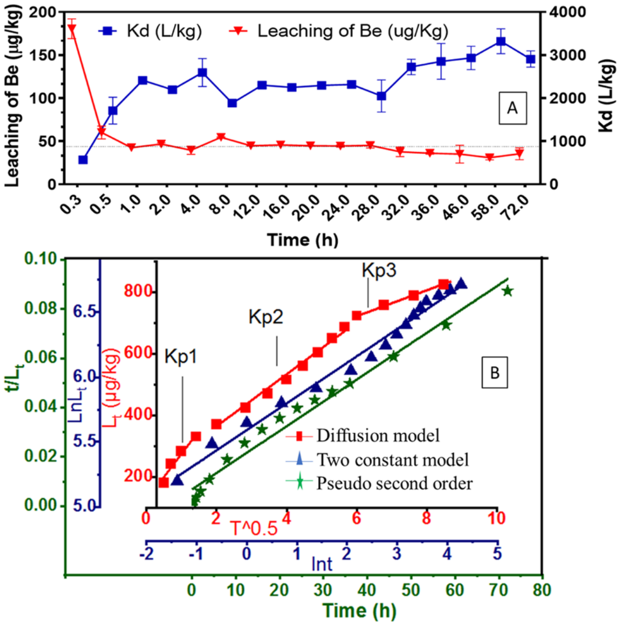

Figure 2. Batch kinetics of Be desorption using SARS. (A) Amount of leaching at different time (h) intervals; (B) Different kinetic models of Be leaching. The models were fitted with cumulative desorption data of Be from LFLS soil.

The plot of the diffusion model using Be desorption data showed three discontinuities in the slope (Figures 2B and S1), which represents the desorption of Be involving three different diffusion controlled mechanisms. In the first phase, the diffusion rate constant (K_{p1}) was very high (157 μg Be/kg $h^{0.5}$, R^2 = 0.955), while slower desorption occurred in the second (K_{p2} = 87.1 μg Be/kg $h^{0.5}$, R^2 = 0.987) and third phases (K_{p3} = 40.4 μg Be/kg $h^{0.5}$, R^2 = 0.999). The first and fastest desorption was attributed to the dissolution of Be from the boundary layer of the soil−solution interface (Figure 3), where Be was weakly bound after spiking. The weakly bound Be would be available for interactions with anions and displaced by competition with cations present in the SARS. The slow desorption rate in the second step (the overall rate-controlling step) resulted from the diffusion of Be from the exterior of the soil pores along the pore wall surface. Subsequently, Be in the interior of the pores or entrapped in meso-/micropores were very slowly desorbed, after which equilibrium is reached, and

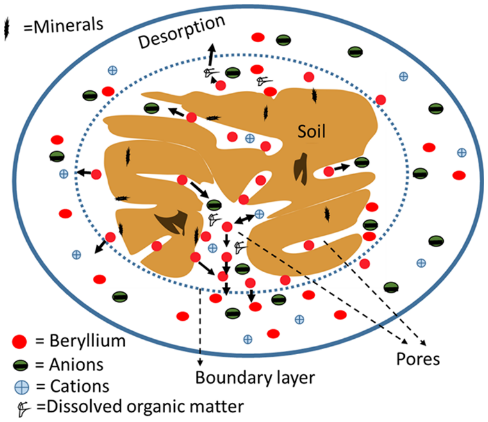

Figure 3. Conceptual modeling of Be desorption from the LFLS soil.

$L_{t(\max)}$ of Be was found to be 556 μg/kg under the experimental condition. Islam et al.[13] reported the sorption process of Be from soils under three diffusion-controlled mechanisms, which is a similar mechanism as the reversible sorption (desorption) mechanism observed in this study. A conceptual model of Be desorption has been depicted in Figure 3, which was adopted from the concept of reversibility of the sorption process.[13,43,44]

Because the desorption mechanism of Be was not entirely diffusion-controlled (as the plot q_t vs $t^{0.5}$ is not linear and not passed through the origin),[43] it rather involves a multistep mechanism (as discussed above); therefore, other models may also be applied for interpreting the data. Using a pseudo second-order kinetic model, the Be desorption rate constant (K_2) was 0.000212 kg/μg h (R^2 = 0.977), and this model is often useful for the materials containing multiple reaction sites and indicates that the initial reaction is rapid and reaches equilibrium quickly and then continues the sorption/desorption with a slow reaction,[45] which is consistent with the above discussion. Moreover, the initial desorption rate constant (a) and desorption rate coefficient (b) of Be were 384 μg Be/kg h and 0.259 μg Be/kg, respectively, as determined by the two constant model.[46]

From the thermodynamic study, we found a negative value of enthalpy ($\Delta H = -0.0205$ kJ/mol), which represents that the desorption reaction was enthalpically influenced (exothermic in nature) and a positive value of entropy ($\Delta S = 0.0558$ kJ/K mol), suggesting favorable reversible sorption by increasing the randomness of the solid-solution interphase.[46,47] If ΔH is negative and ΔS is positive, then the negative value of ΔG at any temperature is expected (always thermodynamically spontaneous and favorable reaction),[47,48] which was also found in this study for Be desorption, resulting ΔG values of −16.1, −16.6, −17.2, and −17.8 kJ/mol at the temperature of 288, 298, 308, and 318 K, respectively. Therefore, the desorption process of Be was spontaneous and enthalpically as well as entropically influenced. Alghanmi et al.[46] reported that a negative value of ΔG and positive value of ΔS showed high affinity of metal ions toward leachate solution and indicated spontaneity of the desorption process, which is consistent with this study for Be.

2.3. Desorption-Speciation of Be Using Sequential Leaching (BCR Procedure). The desorption of total Be in each BCR sequential leaching fraction was F1 = 33−68%, F2 = 17−35%, F3 = 5−15%, and F4 = 5−35% using LFLS soils at different conditions including spiked and natural soils and dependent on the incubation period after spiking the soils with Be (Figure 4). The relatively higher extraction of Be in F1 reflects the presence of more labile, environmentally available, and readily bioavailable species that were linked with carbonates, secondary minerals, or very weakly adsorbed to minerals and mineral surfaces[24,49] and soil pores[13] after spiking. Relatively lower desorption of Be occurred from oxyhydroxide of Al/Fe/Mn in the F2 fraction, from organic substances and sulfides in the F3 fraction,[11,24,50] which are suggested to be potentially bioavailable. The residual phase (F4) represents the most consolidated or inert phases in the form of the lattice of silicate minerals,[11] metallic alloys,[50] congealed oxide and co-precipitated strongly bonded complexes[49] which are resistant to decomposition by biological, geochemical, or hydrological processes. This fraction contained a relatively higher amount of Be in natural soil but varies in the spiked soil depending on the soil types, incubation times, and effect of temperature on transformation of minerals or surface chemical interaction.

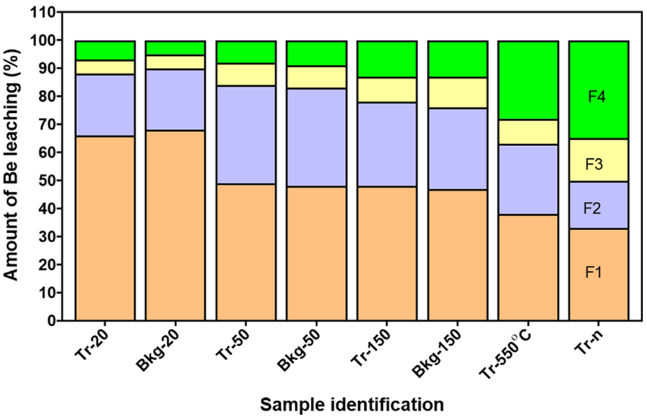

Figure 4. Effect of incubation time (20, 50, and 150 days) and heat treatment on the desorption and migration of Be. Here, F1, F2, F3, and F4 are the first, second, third, and fourth fractions of the Be desorption from sequential leaching. Tr and Bkg represent trench and background soil; Tr-*n* and Tr-550 °C indicate trench soil at its natural condition (unspiked) and under heat treatment at 550 °C (spiked), respectively. There is no statistically significant difference ($P > 0.05$) of the Be desorption from the trench and background soils.

2.3.1. Effect of the Incubation Period and Temperature on Be Desorption. The amount of Be (%) associated with the more available fractions F1−F3 decreased sharply with the increase in incubation period from 20 to 150 days (Figure 4), with a corresponding increase in the fraction F4. This change was significant ($P < 0.05$), particularly in the heated (550 °C) soil, resulting in the amount of Be extraction being similar to the natural soil. This result shows the extent of ongoing incorporation of Be into more resistant phases with the passage of time, with an additional amplified aging effect derived from thermalization. Therefore, with the increase in incubation time, the binding affinity of Be increases with geochemically reactive elements (organic/inorganic) of soil, inner (diffusion in the pores) and outer-sphere complexation in the amorphous and crystalline minerals.[13] There is a significant difference ($P < 0.05$) of Be desorption between the fractions except for F3 and F4 for 20, 50, and 150 days (Figure 4). We found a strong linear regression relationship (R^2 = 0.832−0.999) in the desorption fraction of Be from F1 to F3 as a function of incubation time, temperature, and natural soil condition

(Figure S3). Thermalization significantly ($P < 0.05$) decreased the desorption in the readily bioavailable (F1) and potentially bioavailable (F2 and F3) fraction with a corresponding increase in the consolidated/inert fraction (F4). Saradhi et al.[2] also reported the stabilization of Be in red-mud using thermalization. Therefore, increasing the contact period of Be with soil in the field condition and thermalization can be expected to reduce Be desorption and migration.

Although the laboratory aging experiments and heat treatment cannot accurately simulate the natural environmental conditions, the results reported in this study using these types of techniques can offer important insights into the long-term behavior of contaminated sites such as LFLS, particularly into the changes of contaminant−surface interactions associated with mineral aging[51] or due to the influence of mineral re-crystallization and transformation (details in Section 2.3.4).

2.3.2. Effect of Soil Types on Be Desorption. Figure 5 represents the interaction of Be with various soils and comparative desorption, including sandy loamy (trench and background from LFLS), vertisol, and calcareous soils as measured by the sequential leaching of BCR technique. The extractability of Be from soil decreased in the order sandy loamy (50%)> calcareous (43%)> vertisol (20%) [such as the solubility order of Al (Table 2), representing the association of Be with this element and solubility at low pH] in the readily bioavailable fraction (F1), which reflects relatively higher risk of Be arising from higher desorption, and transportation or bioavailability in sandy loamy and calcareous soils than the vertisol soil. The amount of desorption was different in F2 [vertisol (56%)> calcareous (45%)> sandy loamy (36%); similar order of Ba solubility, and DOC], F3 [vertisol (26%)> calcareous ≈ sandy loamy (8.5%); similar order of Ba solubility], and F4 [almost similar for all soil, 6−9%].

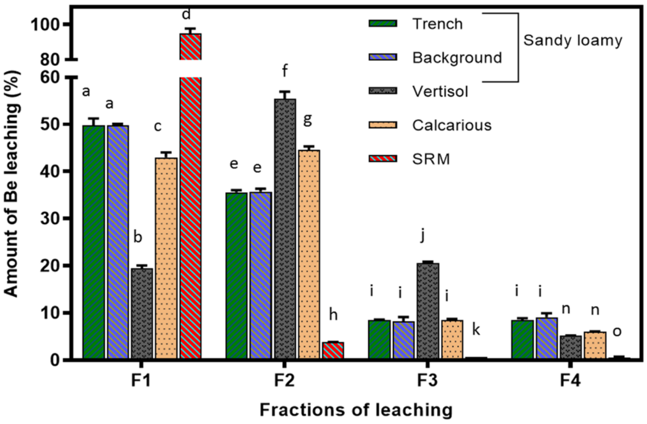

Figure 5. Desorption of Be using sequential leaching from different soils [("vertisol" and "calcereous" soils were collected from south of Dubbo and near Coolah, NSW, respectively; all samples were 50 days spiked except SRM (loamy clay 1)]. Similar letters (e.g., e and e or i and i) represents no statistically significant difference among the variables.

Relatively higher desorption in F2 and F3 from vertisol soil resulted from higher oxyhydroxide of metal and organic matter in that soil.[52,53] Interestingly, Be showed a relatively stronger interaction with the vertisol soil (strong oxyhydroxide/clay-organic complexation), resulting in lower desorption in the readily bioavailable fraction. Higher metal sorption and limited desorption in the presence of vertisol soil (clay-rich) was also reported for other metals.[52,53] Beryllium in sediment is primarily adsorbed to the clay minerals,[54] and Edmunds[7] reported the interaction of Be in the order clay and shales > sandstone > limestone regarding different sedimentary rocks. Though the LFLS site soil is sandy loamy, the waste trenches in the study site were covered by a 1 m clay/shale layer,[55] which could play a significant role in the reduction of Be desorption and migration, and may explain the relatively minor releases of Be from the waste trenches at the LFLS. It is, therefore, possible that at other Be-contaminated sites related to industrial or Be research facilities, the application of the clay-rich soil or vertisol soil could provide an effective encapsulation to reduce Be migration or transport in the environment, although this would require further site-specific research in each case.

2.3.3. Solution Phase Analysis. Variation of different electrochemical properties (pH, EC, and ORP) during sequential leaching (Table 2) is linked with accelerating metal (e.g., Be) desorption and transport, resulting from the oxidation/degradation of metal sulfides and organic matter.[49] The results (Table S4) showed a negative correlation between ORP and Be solubility [r = −0.668 (LFLS); r = −0.818 (calcareous); and r = −0.907 (vertisol)]. In soil, organic matter is the primary source of the electron to balance reduction reaction,[56] and we found a linear regression (R^2 up to 0.996) relationship of ORP, DOC, and solubility of Fe and Mn with

Table 2. Data of Solution Phase Characterization from Sequential Leaching[a]

	LFLS			calcareous			vertisol		
	F1	F2	F3	F1	F2	F3	F1	F2	F3
pH	3.14	2.23	1.75	3.19	2.07	2.14	3.72	2.67	2.12
EC (mS/cm)	0.731	33.3	68.0	0.489	30.0	50.5	0.875	28.9	49.6
ORP (mV)	333	126	474	451	190	531	345	143	407
DOC (g/kg)	−0.640	0.903	189	−0.631	0.479	4.54	−17.0	0.608	−136
Be (mg/kg)	3.82	1.89	0.527	3.25	3.94	0.763	1.10	5.03	1.96
Al (mg/kg)	547	1607	2676	102	145	131	87.3	145	133
Fe (mg/kg)	35.5	1015	2133	60.7	101	74.7	1.43	826	178
Mn (mg/kg)	69.5	28.5	9.69	97.9	312	10.2	8.19	11.2	8.44
Ba (mg/kg)	17.5	22.1	5.14	9.02	52.1	2.70	22.5	156	39.8
P (mg/kg)	181	209	33.3	20.3	35.6	7.05	35.3	35.1	63.9
S (mg/kg)	50.9	125	902	99.8	148	22.3	153	133	240

[a] pH (in Milli-Q water) of LFLS, calcareous, and vertisol soils were approximately 6.06, 7.97, and 8.14, respectively.

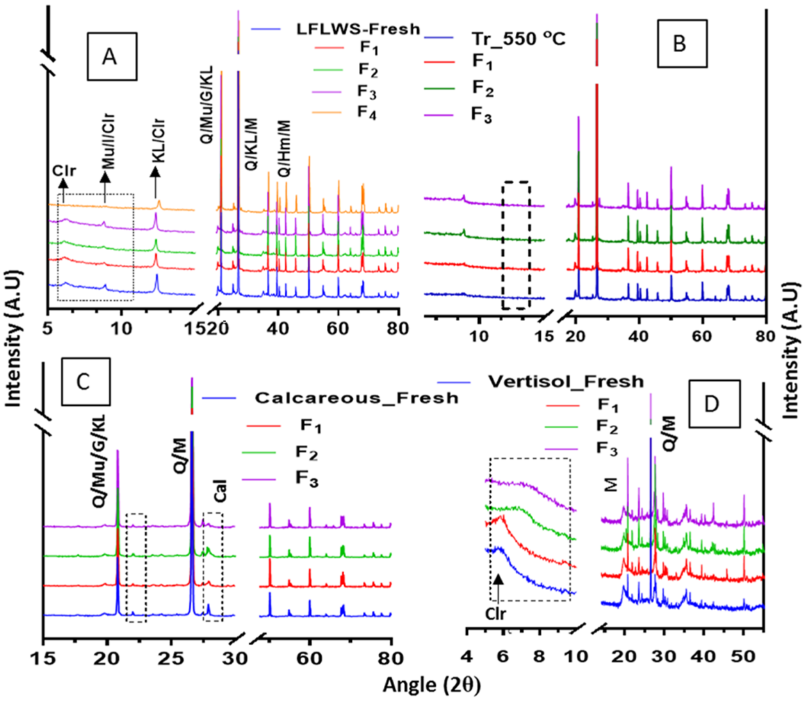

Figure 6. Effect of mineralogy on Be desorption from different soils during sequential leaching. (A) LFLS soil; (B) preheated (550 °C) LFLS soil; (C) calcareous soil; and (D) vertisol soil. The rectangular region highlights small changes in the peaks. Here, Q = quartz (silicon oxide-alpha), KL = kaolinite, Clr = chlorite, G = goethite, Hm = haematite, M = magnetite, Mu = muscovite, I = illite, and Cal = calcite.

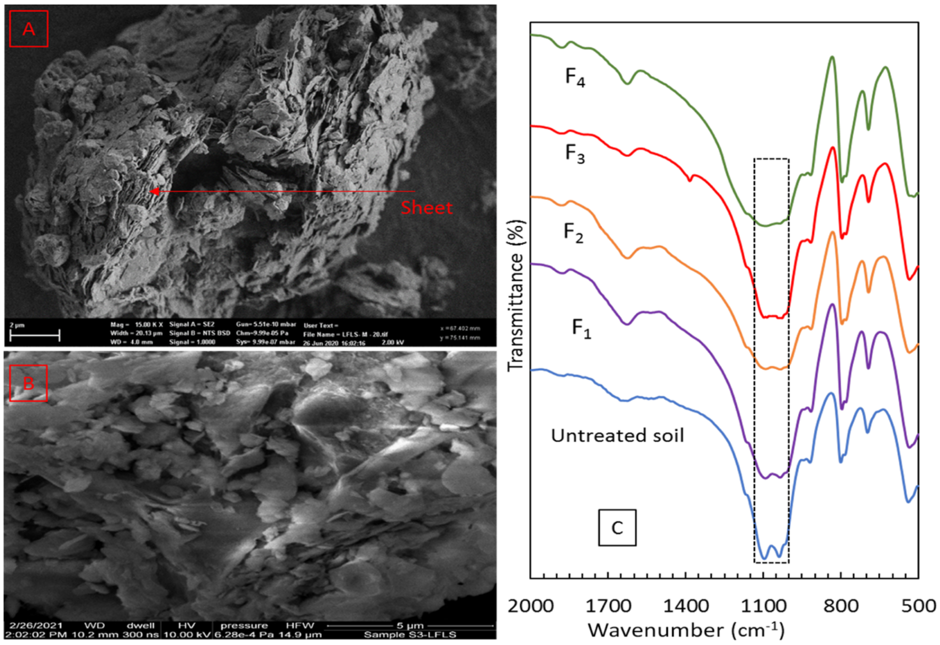

Figure 7. SEM images of (A) untreated LFLS soil (showing some sheet or plate-like morphology probably for kaolinite and chlorite) and (B) thermally (550 °C) treated soil (showing disappearance of the sheets); (C) FTIR spectra indicating bond types (functionality) of Be in each step of the BCR sequential leaching process.

Be solubility (Table S4). However, Be is less sensitive or not directly related to the ORP due to its single oxidation state (+2), but some researchers in other fields reported that ORP influences Be solubility,[57,58] which recommends further study of the role of redox processes on Be solubility in soil.

Relatively, higher amounts of Al, Fe, Mn, Ba, P, and sulfur (S) solubility were noticed in the solution phase of different desorption fractions (Table 2). Zhang et al.[40] reported that Be solubility correlated with Al concentration due to their similar electrochemical properties (electron affinity of Be^{2+} and Al^{3+} are 6.45 and 6.00, respectively), which was also found in this study (Table 2). A previous study reported that oxyhydroxides of metals influence Be sorption,[13] but Be may also be desorbed at low pH,[14] which has also been reflected in this study, resulting in some regression relationship with Be desorption [with Mn (R^2 = 0.674), Ba (R^2 = 0.323), P (R^2 = 0.707), Ca

($R^2 = 0.802$), K ($R^2 = 0.781$), and Sr ($R^2 = 0.578$)] (Table S4). Strontium (as ^{90}Sr) is also a contaminant of potential concern in LFLS soils, and the migration behavior of Sr at the site was recently reported.[59] This current study showed a significant ($P < 0.05$) regression relationship between Be and Sr desorption (Tables S3 and S4).

2.3.4. Solid Phase Characterization. From the XRF data (Table S5), the amounts of different metals (Al_2O_3, Fe_2O_3, MnO, BaO, K_2O, and V_2O_5) and nonmetals (P_2O_5, SO_3) in the solid phase were found to decrease after sequential leaching of Be from fresh soil to F1 to F4, which corresponds with the data of solution-phase analyses. The residual phase contained most of the Si and Ti.

From the XRD analysis of each solid fraction resulting from the sequential leaching (Figure 6), there were no significant changes of the crystallographic phase, but rather small changes (shifts or decreases of the intensity of the XRD peak of chlorite, kaolinite, calcite, illite, muscovite, and goethite) in the regions <30° (2θ angle). These results suggest that Be, along with other elements, was released from the outer sphere of minerals/clay, amorphous oxyhydroxide of metals, and interior or exterior pore or pore wall surface without significantly affecting the crystalline phase of the soil. The desorption study after thermalization (550 °C) clearly demonstrated (Figure 6B) the loss of the kaolinite and chlorite peaks, which could be an indication of the transformation of unstable mineral phases over time, and temperature and stable phases are also left, which resulted in lower desorption. At a temperature of 550 °C, kaolinite destruction and loss of chlorite due to dehydration was reported previously,[60] and this thermalization is sometimes used for explaining the weathering of minerals from soils.[60,61]

There was no noticeable change in the soil morphology (as determined by SEM) in the F1 and F2 (Figure S4), but a noticeable change was found in the fractions F3 and F4 due to the more extreme conditions. Thus, the predominant association of Be in fractions F1 and F2, which represents Be, together with other elements was released into the solution from the surface of minerals, surface oxyhydroxides of metal, and the exterior of soil pores or pore wall surface, without affecting the soil morphology. However, a substantial change in the morphology was found following heat treatment (550 °C), including the loss of some sheet or plate-like structure (Figure 7A,B), which probably consisted of kaolinite and chlorite,[62] which supports the XRD data.

The untreated (spiked) soil showed two distinct FTIR peaks at 1092 and 1034 cm^{-1}, which could be attributed to the presence of Be−O/OH bonds (i.e., associated with oxyhydroxides of metals or organic functional groups in soils), as similar information was also reported in the literature.[13,63,64] A significant flattening of the FTIR peaks (at 1092 and 1034 cm^{-1}) was found after the desorption (using sequential leaching) of Be from the spiked soil to F1 to F4 (Figure 7C), which could be attributed to the splitting of Be−O/OH bonds in soils during the leaching experiment. Islam et al.[64] reported that the addition of Be in the LFLS soil resulted in developing two FTIR peaks at 1092 and 1034 cm^{-1}, which disappeared after the desorption of Be using bioaccessibility extraction, which is consistent with this study for the sequential leaching process. However, Fe−O−H, Al−O−Si, Si−O−Si, and Si/Al−O bonds are also present at around 450−1200 cm^{-1}, as reported in the literature.[13,63,65] Specifically, Krivoshein et al.[65] reported Si−O stretching vibration (quartz and clay minerals) at 1020−950 cm^{-1}; (Mg/Al)−OH vibration (illite and smectite minerals) at 950−600 cm^{-1}; and iron oxides at 700−600 cm^{-1}, and minor shifts of the peaks at around 916, 796, 692, and 536 cm^{-1} were found after Be desorption, which suggests the dissolution of Be with other elements during sequential leaching.

2.4. Implications for the Environmental Risk of Be.

The enrichment factor (EF) is usually used to express the metal contamination and toxicity caused by natural as well as anthropogenic sources[24,66] (details in the Supporting Information). The calculated value of EF was 2.5×10^{-5} to 4.1×10^{-5} for natural soil, which indicates that Be was not enriched in the soil (as EF < 1)[24] from the waste trenches (anthropogenic sources) after more than 5 decades since disposal. However, the potential for risk in the future may arise from desorption and subsequent leaching of Be from the waste trenches, as indicated by our leaching data for the LFLS soil. The desorption of Be (0.004−0.101 μg/L) from natural soil in all leachates (SARS, MWEP, SPLP, and TCLP) did not exceed the maximum permissible concentration (MPC) value (<0.13 μg/L) and was well below the ecological serious risk concentration (SRC_{ECO}) value (<51 μg/L).[31] These data indicate that Be in the present field soil condition does not represent a significant risk of groundwater contamination and ecological impact. Limited desorption and, therefore, immobilization of Be within the natural LFLS soils was also substantiated with very high K_d values (7990−139,250 L/kg).

However, in the case of simulated contaminated (spiked) soil (batch leaching), the concentration of Be (1.6−18 μg/L) exceeded the MPC, though it remained below the SRC_{ECO}, reflecting that the potential ecological risk could be imposed if the concentration of Be increases due to the release of Be from the waste trenches. In the case of sequential leaching, the concentration of Be in the readily bioavailable (3.73 μg/L) and potentially bioavailable (1.3−1.9 μg/L) fraction from the natural soil exceeded the MPC value but was less than SRC_{ECO}. For all spiked soil, the Be in the readily bioavailable fraction (60−105 μg/L) was beyond the MPC and SRC_{ECO} values except the vertisol soil (27.3 μg/L), which indicates the potential importance of vertisol soil for reducing the risk from Be desorption and migration.

However, $P_i = 0.03−0.77$ for all batch leaching, and $E_r = 6.6$ for sequential leaching data using natural soil (Figure S5A,B), indicated no contamination and potential ecological risk (as $P_i \leq 1.0$ = no contamination and $E_r < 40$ = no potential ecological risk)[67,68] of Be in its current situation (see the Supporting Information for details), but the risks may be imposed for contaminated (spiked) soil under the different circumstances represented by the leaching solutions. In addition, the leachate concentration (batch + sequential) from both spiked and natural soil was below the Australian drinking water guideline value (60 μg/L) for Be,[30] which was surpassed only by the readily bioavailable fraction of soil incubated for 20 days, which suggests that longer residence time of Be in the soil could reduce the desorption and ecological and human health concern.

Cendón et al.[32] studied groundwater hydrochemistry of the LFLS area and reported limited mobility of Be at neutral pH; however, the potential for mobilization exists under acidic and alkaline conditions.[54] We found some desorption and migration behavior of Be from the LFLS soil under acidic pH conditions. The properties of LFLS soil (low CEC and high Al, Fe, and Mn in the leachate)[13] are indicative of strongly

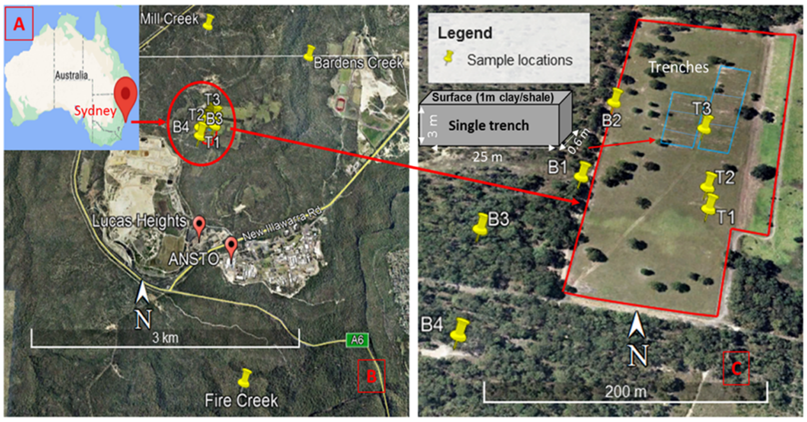

Figure 8. Study area (trench area highlighted) of LFLS, including locations of soil samples (Google Earth, 2018).[69] (A) Study area near Sydney; (B) sample location and surrounding area of Lucas Heights; and (C) collected samples from the trench area. The letters "T" and "B" represent trenches and background soils [total seven samples were collected including T1 = surface soil furthest from the trenches; T2 = surface soil down gradient from the trenches; T3 = soil from on top of the trenches; B1 = reference background soil; B2 = test trench background soil; B3 = soil from the west side of the fence background; and B4 = south background soil (outside of the fence)].

weathered soils, which have higher mobility of metals,[27] and therefore, Be in soil may be mobilized by chemical weathering. Therefore, insights into the desorption of Be in different soils provides an important basis for further research on managing risk given the toxicity of Be at relatively low concentrations.

3. CONCLUSIONS

This study revealed relatively lower Be desorption in the presence of inorganic leachate than in the organic leachates representing Be complexation, and subsequent solubilization might be accelerated in the presence of an organic acid. This is a significant finding given the presence of organic complexants at LFLS and potentially other similar sites. Moreover, the higher amount of Be desorption using SARS than SPLP demonstrated the importance of considering local rainwater compositions. The kinetics of Be desorption indicated that the initial desorption rate was rapid, and subsequently, slower desorption occurred, which was well described by three diffusion control mechanisms. The thermodynamics of desorption revealed that the desorption process was, spontaneous ($\Delta G < 0$) at any temperature, and enthalpically as well as entropically influenced.

Sequential leaching using the BCR technique indicated the desorption of Be in various fractions depended on soil conditions and soil types. Increasing the incubation period (20−150 days) and heat treatment (550 °C) of the LFLS soil reduced Be desorption in F1−F3 significantly ($P < 0.05$). Beryllium in the readily bioavailable fraction (F1) was substantially lower in the vertisol soil (20%), which implies vertisols or clay-rich soils could be applicable for the effective encapsulation of Be in the environment. Solid and solution phase analysis suggested that the desorption of Be was regulated by different electrochemical properties (e.g., pH and ORP), dissolution of soil organic matters (e.g., DOC), oxyhydroxides of metals or inorganic (Al, Mn, Ba, Zn, Sr, Ca, K, and P) elements, reactive surface of clay minerals, and soil pores.

Based on the measured K_d (high value), risk index values (EF, P_i, E_r), and in comparison with the guideline values for Be for surface water and groundwater, no significant ecological risk and human health concerns should arise from the desorption of Be from LFLS soils in the present situation at the site. However, potential risk could result, depending on the soil conditions, particularly if Be concentrations increase in the site soil due to migration of Be from the waste trenches, with ground water acidification or other metal mobilizing factors.

4. MATERIALS AND METHODS

4.1. Study Area, Sample Collection, Preparation, and Characterization.

The LFLS is a waste disposal site located within the buffer zone boundary of the Australian Nuclear Science and Technology Organisation (ANSTO) at the southern periphery of Sydney, Australia (Figure 8).

In the 1960s, according to standard practice at the time, low-level radioactive waste with a significant amount of Be (~1070 kg) was disposed in unlined trenches at the LFLS.[38] Contaminants including Be have the potential to be released to the surface soil and impact the environment, surrounding local ecology, and potentially human populations. This site has been described in previous studies[13,55] (further details in the Supporting Information). Soil samples (0−10 cm) were collected from the trenched area (samples T1−T3), and background samples (B1−B4) from the vicinity of the LFLS. All the soils were dried, homogenized by grinding, sieved (<2 mm), and stored for further experiments.

At present, the concentration of Be in the soils investigated is low (0.39−0.66 mg/kg),[13] but there is the potential for it to be increased in the future through the release of Be from the waste trenches. To represent a potential moderate increase of Be in soils, the soil samples were spiked with 10 mg of Be/L solution (0.6 mL/g soil) and incubated for 20, 50, and 150 days at 60% water holding capacity (field capacity).[64] The total amounts of Be in the soils (spiked Be and pre-existing Be in the natural/field soil) were determined using microwave acid digestion,[70] followed by inductively coupled plasma mass spectroscopy (ICP−MS, PerkinElmer, USA). All reagents and chemicals used in this study were of analytical grade (see Supporting Information).

4.2. Desorption of Be Using Batch Leaching Experiments.

Batch leaching experiments were conducted in the presence of major anions and cations that have been reported to be present in acidic rainwater of the Sydney region [chloride (Cl^-) = 4219 μg/L; sulfate (SO_4^{2-}) = 1162 μg/L; nitrate (NO_3^-) = 843 μg/L; sodium (Na^+) = 556 μg/L; magnesium

(Mg^{2+}) = 74.1 μg/L; calcium (Ca^{2+}) = 180 μg/L; potassium (K^{+}) = 86.0 μg/L; and ammonium (NH_4^{+}) = 336 μg/L]. The compositions of the SARS (pH 4.5) were adopted from the following literature[71−75] (Table S6). The Be desorption results using SARS were compared with various standard batch leaching processes, including MWEP (ASTM D 3987-85), SPLP (EPA 1312), and TCLP (EPA 1311). The leaching procedures were adopted from the literature[15,16,19] (details in Table S7).

The TCLP extraction represents acidic landfill leachate and is applicable to management decisions for the disposal of waste and determination of whether the waste is hazardous. The TCLP reagent contains acetic acid (see the Supporting Information for details), which is important to determine the effect of organic acid on Be desorption and migration. Organic acids arising from the degradation of organic matter and compounds influence metal desorption and transport.[35] The co-disposal of organic wastes in the LFLS trenches[76,77] and the presence of several municipal organic waste disposal sites adjacent to the LFLS[32] might be influential on the Be mobility; therefore, it is of interest to examine Be desorption using TCLP leachate. All leachate solutions in this batch leaching process were mixed with contaminated soils (1:20 ratio, soil/solution), shaken in an end-over-end shaker at 60 rpm (18 h, 23 ± 2 °C), centrifuged (4500*g*, 15 min), and filtered (0.45 μm), and the amount of Be in the leachate was analyzed using ICP−MS.

The distribution coefficient (K_d) is an effective tool for demonstrating the relative distribution or migration of the contaminant (e.g., Be) in the environment.[13] The K_d (L/kg) of Be was calculated according to the equation below[78]

$$K_d = \frac{q}{C} \tag{1}$$

where q (μg/kg) and C (μg/L) are the amounts of Be present in the solid and liquid phase, respectively.

4.3. Batch Leaching Kinetics and Thermodynamics.

Different batch leaching methods were conducted for a fixed time period (in most cases, 18 h) at room temperature and assumed to have reached equilibrium, although it is recognized that 18 h may not be sufficient time for equilibrium to be reached.[18] Therefore, a serial batch leaching study of the kinetics of Be desorption from LFLS soil using SARS was adopted from Neupane and Donahoe,[79] and conducted at 1:20 (solid/liquid) ratio for 3 days with samples taken at successive time intervals (0.25, 0.5, 1, 2, 4, 8, 12, 16, 20, 24, 28, 32, 36, 46, 58, and 72 h). The temperature may also be an influential factor for batch leaching of metals,[46] particularly given the possibility of a significant seasonal variation. Therefore, the thermodynamics of desorption was studied at 318, 308, 298, and 288 K temperature for 24 h using SARS (as above).

The supernatant was collected (∼10 mL) from each step, followed by centrifugation (4500*g* for 15 min at 10 °C) and filtration (0.45 μm). The rest of the supernatant was discarded carefully, and 20 mL of fresh SARS was added as before, and the procedure continued up to 72 h. Before sampling from each batch, the pH and electrical conductivity (EC) were recorded. The concentration of Be in each step was measured by ICP−MS. DOC and other elements were also measured according to the method described in a previous study.[79] Mass loss (<5%) was calculated after completing the whole leaching cycle.

The generated data of desorption kinetics were fitted with different kinetic models, including the intraparticle diffusion model, two-constant rate model, and pseudo second-order kinetics model according to the following literature[44,46,80] (refer to the Supporting Information for details) to evaluate the mechanism of the desorption reaction over time. The desorption maxima ($L_{t(\max)}$) of Be under the experimental condition was measured according to the previous study[45] (details in the Supporting Information). Thermodynamic parameters, including the changes of Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated according to the literature[46] (details in the Supporting Information).

4.4. Factors Influencing the Desorption-Speciation of Beryllium Using Sequential Leaching (BCR Procedure).

The desorption and transport of metals (e.g., Be) from the LFLS and similar sites is largely dependent on the types of soils where they are deposited. This mobility within the soil profile may change over time, and these processes have been investigated by various authors.[80−83] In this context, the modified BCR sequential leaching procedure[23,50] was applied (details in Supporting Information, Table S8) for determining the effects of different factors, including incubation period (20−150 days), soil types [sandy loam[13] (collected from LFLS), calcareous, and vertisol soils were collected from the south of Dubbo and near Coolah, NSW, respectively, for comparison], and temperature (thermalization) on the desorption of Be. After shaking the soil/solution mixture for a specified period for each fraction (F1, F2, F3, and F4), the pH, EC (Mettler−Toledo, China), oxidation−reduction potential (ORP) (Hanna, USA) were recorded just prior to centrifugation, and the amount of Be desorption was measured after centrifugation and filtration followed by ICP−MS. Leachability and potential stabilization (immobilization) of Be from the solid waste (red mud) by thermalization (500 °C) were reported previously.[2,20] Therefore, we followed a similar procedure in which we preheated the spiked soil samples (550 °C, 3 h in a muffle furnace) and performed sequential leaching to evaluate how thermalization affects the amount of Be speciation in each fraction.

The solution phases of each of the sequential leaching fractions were analyzed, including different electrochemical properties (pH, EC, and ORP), DOC (TOC-L analyzer, Shimadzu, Japan), soluble metals and nonmetals (ICP−MS/OES). The solid phases were also investigated for mineralogical changes by X-ray diffraction (XRD, Cu Kα radiation), changes of elemental composition by X-ray fluorescence (XRF), surface morphological changes by scanning electron microscopy (SEM, Zeiss Sigma VP FESEM, Germany), and any changes of Be−O/Be−OH bonds in the solid samples were studied by Fourier transfer infrared spectroscopy (FTIR, Agilent) (details in the Supporting Information).

Different risk assessment parameters were determined using the leaching data, including EF, which is used to determine metal contamination or toxicity in the soil comparing with its background metal concentration;[24] pollution index (P_i), used to determine the degree of toxicity using metal concentration in the batch leachate;[67] and coefficient of potential ecological risk (E_r) are used for sequential leaching[68,84] (details in the Supporting Information). Moreover, desorption data were also compared with various standard guideline values of surface and ground water[10,30,31] for assessing ecological and human health concerns.

4.5. Quality Control and Data Analysis. All experimental samples were run as duplicates, and duplicate blank samples were also run for every batch of the experiment. The data were validated by running the experiment simultaneously with a standard reference material (SRM) (loamy clay 1). The extraction solutions were prepared and completely homogenized by ultrasonication, and the pH was adjusted and allowed to stabilize. For all the experiments, the pH was monitored and checked at the end of the extraction. To address possible matrix effects, ICP−MS standard solutions were prepared with corresponding individual chemical compositions. The deviation of the continuous calibration verifications were accepted ±1 μg/L, and internal standard recovery was 90−110%. The software programs Excel, Graph pad prism8, and Origin pro (2021) were used for plotting the graphs and statistical data analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04572.

> Description of the study area; compositions of all leaching solutions (batch and sequential) and experimental conditions; equation of thermodynamic and kinetic models for leaching data; details of the instrumental and analytical conditions; equation for environmental risk implication; details of the desorption data of Be; data of correlation analysis; XRF images; and SEM and SEM−EDS images (PDF)

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Notes

The authors declare no competing financial interest.

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