Supplementary Material

Table S1 Chemical components and *in vitro* parameters for the PBET, ALF and MGS bioaccessibility tests.

method [a]	phase	component [b]	parameters		
			pH	liquid/solid ratio /(mL·g^{-1})	extraction time /h
PBET	gastric	1.25 g of pepsin, 0.5 g of sodium citrate, 0.5 g of sodium malate, 420 μL of lactic acid, 500 μL of acetic acid	1.3 [c]	100:1	1 h
	intestinal	0.07 g of bile salt, 0.02 g of pancreatin	7.0	100:1	3 h
ALF	lung	0.05 g of $MgCl_2$, 3.21 g of NaCl, 0.071 g of Na_2HPO_4, 0.039 g of Na_2SO_4, 0.128 g of $CaCl_2·2H_2O$, 0.077 g of sodium citrate dihydrate, 6 g of NaOH, 20.8 g of citric acid, 0.059 g of glycine, 0.09 g of sodium tartrate dihydrate, 0.085 g of sodium lactate, 0.086 g of sodium pyruvate	4.5	20 :1	24 h
MGS	lung	6.8 g of NaCl, 5.3 g of NH_4Cl, 2.3 g of $NaHCO_3$, 1.2 g of H_3PO_4, 1.7 g of $NaH_2PO_4·H_2O$, 0.63 g of Na_2CO_3, 0.58 g of sodium acetate, 0.2 g of K-acid-phthalate, 0.45 g of glycine, 0.51 g of H_2SO_4, 0.59 g of sodium citrate, 0.29 g of $CaCl_2·2H_2O$, 0.42 g of citric acid	7.4	20:1	24 h

[a] The PBET method was adopted for RM250-38 and RM-38 samples, while the ALF and MGS fluids were only employed for RM38 sample.

[b] 1 L of extraction solution was individually prepared by dissolving all components involved in the PBET, ALF and MGS bioaccessibility tests in the deionized water. [c] pH value was adjusted with 12 mol·L^{-1} hydrochloric acid.

Table S2 The bioaccessibility values of Cu, Pb and Zn in the intestinal phase (pH 7) for sized-fractionated red mud samples ($mg \cdot kg^{-1}$).

element	RM250			RM250-38			RM38		
	1 h	3 h	4 h	1 h	3 h	4 h	1 h	3 h	4 h
Cu	31.83	11.52	4.48	38.14	9.49	2.77	34.56	10.51	2.13
Pb	50.05	20.99	9.87	53.88	19.45	12.47	53.14	14.85	4.37
Zn	371.80	210.85	160.15	223.61	186.52	143.75	76.43	98.50	83.21

Text S1 The detecting procedure for hexavalent chromium in red mud.

Firstly, an alkaline mixture was prepared by mixing 20 g NaOH and 30 g Na_2CO_3 in 1 L deionized water. Then, 87.1 g of K_2HPO_4 and 68 g of KH_2PO_4 was dissolved in 1 L deionized water to obtain a buffer solution (pH 7). The Cr^{6+} concentration in red mud was determined by adding 50 mL of NaOH-Na_2CO_3 mixture solution, 0.4 g of $MgCl_2$ and 50 mL of the buffer solution to 0.1 ± 0.001 g of sample, followed by 25 ^{o}C for 5 min and finally 90-95 ^{o}C for 60 min. After cooling, the digestion samples were filtered through 0.45μm membrane filter (Schleicher & Schuell), and the final pH values were adjusted to 9.0 ± 0.2 with 65% HNO_3. Finally, the Cr^{6+} concentration in solution were measured by an atomic adsorption spectrometer (AA320CRT, Shanghai).

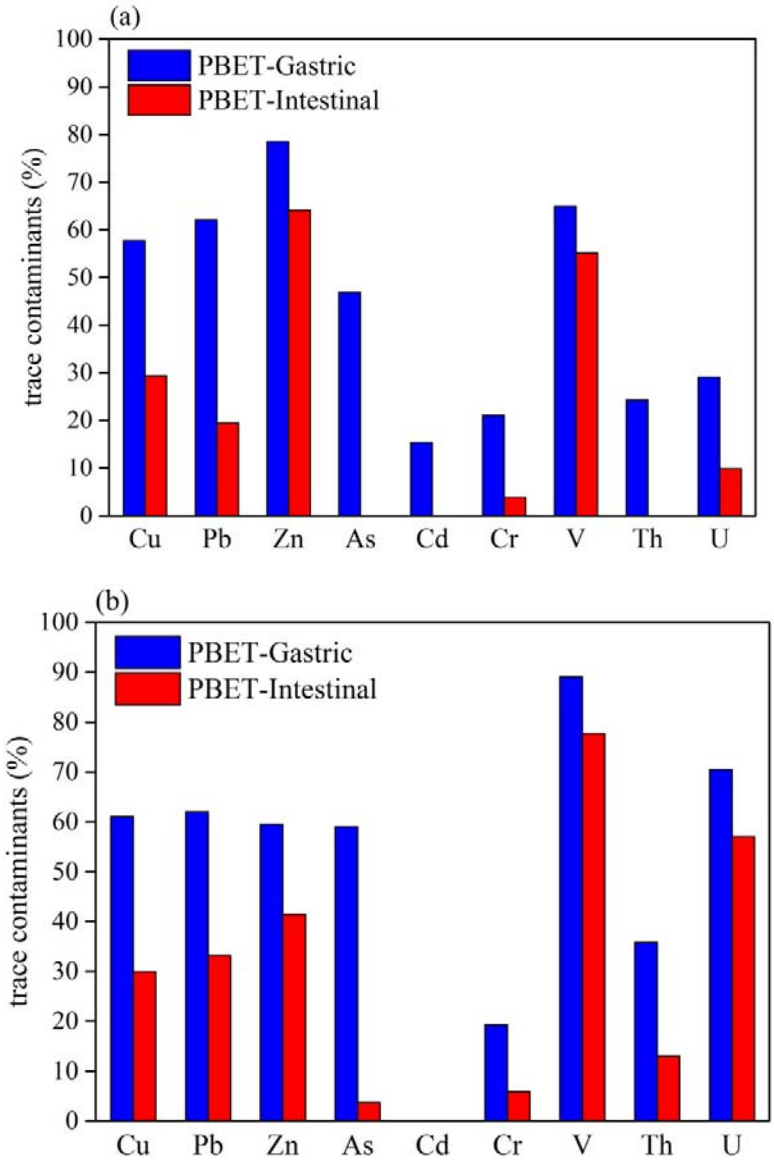

Fig. S1 Percentage of trace contaminants extracted relative to their total concentrations in the precipitates derived from (a) the simulated acid rainwater, and (b) deionized water.

The bioaccessibility percentages of trace contaminants in SAR-Precipitate and DW-Precipitate were calculated from the data in Table 3 using the following expression, respectively:

$$\text{The percentage (\%)} = \frac{\text{bioaccessibility value}}{\text{total content}} \times 100\%$$

Table S3 Percentages of trace contaminants extracted relative to their total concentrations in sized fractionated red mud samples (%).

	element	RM250		RM250-38		RM38	
		gastric	intestinal	gastric	intestinal	gastric	intestinal
heavy metals	Cu	14.71	8.68	15.94	7.14	18.80	8.42
metalloids	Pb	31.53	13.75	29.72	13.46	30.50	11.36
	Zn	37.26	21.58	38.99	35.09	38.67	31.84
	As	7.95	3.92	9.28	3.96	10.21	5.46
	Cd	28.97	20.46	32.82	29.49	18.98	21.65
	Cr	7.01	3.25	6.67	3.03	8.95	3.04
	V	21.02	13.37	15.34	8.29	9.69	5.18
radioactive	Th	5.56	3.07	6.42	5.18	12.15	5.72
elements	U	31.50	25.66	41.85	30.39	58.50	51.67

The bioaccessibility percentage of trace contaminants in >250 μm, 250-38 μm and < 38 μm particle size fractions was calculated from the data in Table 1 and 2 using the following expression, respectively:

$$\text{The percentage (\%)} = \frac{\text{bioaccessibility value}}{\text{total content}} \times 100\%$$

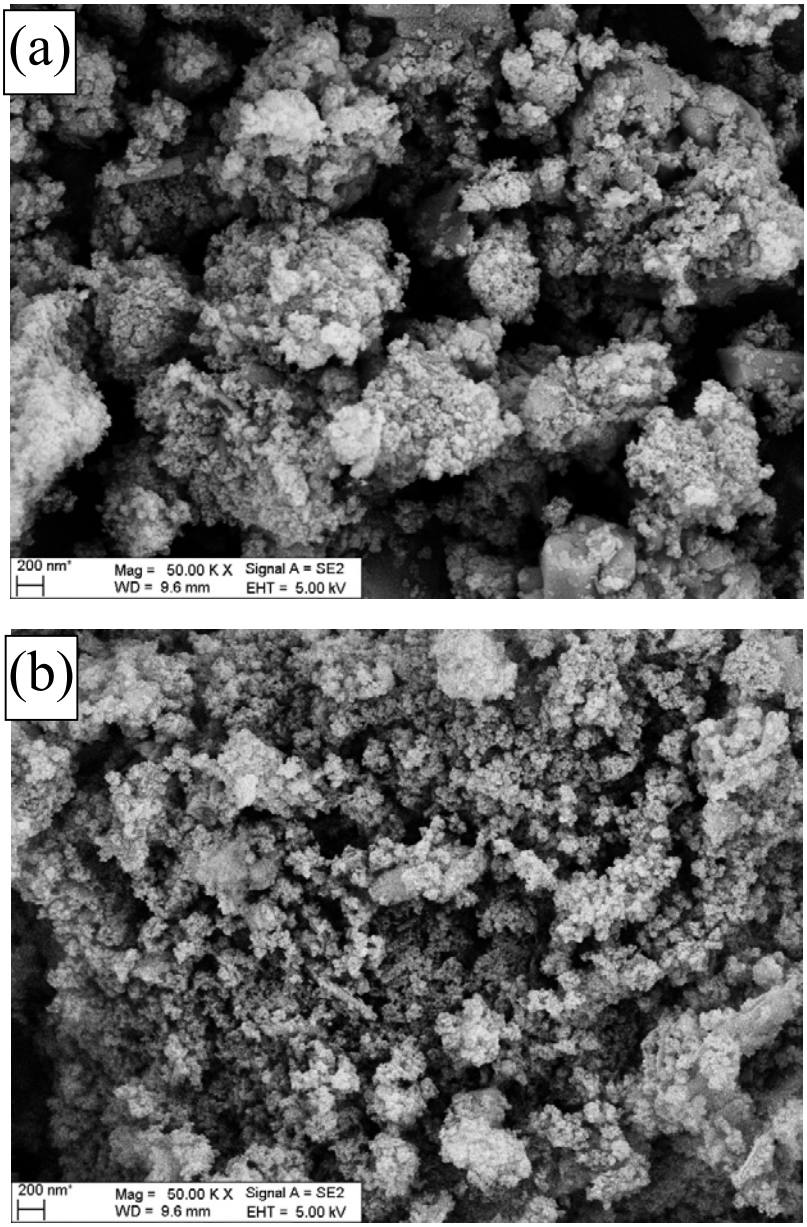

Fig. S2. SEM images of (a) SAR-Precipitate, and (b) DW-Precipitate.

Text S2 Preparation procedure of geopolymeric blocks.

Geopolymeric blocks were synthesized using raw red mud (the representative samples in this study), fly ash, cement and metakaolin as raw materials. Initially, the viscous pastes were prepared by mixing mechanically four raw materials with the activator solution (NaOH solution) to obtain a homogeneous mixture. Secondly, the pastes were molded in plastic cubic molds (40 × 40 × 40 mm), firmly closed by

a plastic cap. Lastly, the closed molds were cured at a required temperature, and then the pastes were demolded and cured again at a required temperature and humidity for a period of time. Total content of trace contaminants in this block were determined using the microwave-assisted digestion. The PBET and leaching tests (short-term and long-term) were performed on a 12 × 12 × 12 mm geopolymeric block, respectively.

It is known to be 3.5 wt% of red mud with respect to total weight of the block. However, the detailed approach and some important parameters cannot be provided for the synthetic blocks according to partners' requirement.

Text S3 Short-term and long-term leaching tests.

Short-term leaching behavior of trace contaminants in geopolymeric blocks was assessed with the TCLP (toxicity characteristic leaching procedure) method, in which two kinds of extraction solutions was used. It was preliminarily determined that the acetic acid extraction solution (pH 2.88 ± 0.05) was more appropriate for the sample. TCLP experiments were performed in a batch stoppered conical flask (50 mL) according to liquid-to-solid ration (20:1, $mL \cdot g^{-1}$), and agitation time was 18±2 h at a 30 rpm constant shaking rate.

0.5 $mol \cdot L^{-1}$ CH_3COOH solution (pH 5) and then nine successive leaching via a simulated acid rainwater (an initial pH 3.0 ± 0.2 adjusted by H_2SO_4/HNO_3 (6:4, wt/wt) mixture solution) were utilized to investigate the long-term leaching behavior of trace contaminants in geopolymeric blocks. According to MEP (multiple extraction procedure) method, each leaching process with the simulated acid rainwater was performed at room temperature for 24 h with liquid-to-solid ratio (20:1, $mL \cdot g^{-1}$), and then the extract was filtered, acidified, and analyzed. The blocks remained from each solid-liquid separation were subject to the identical leaching process with simulate acid rainwater.

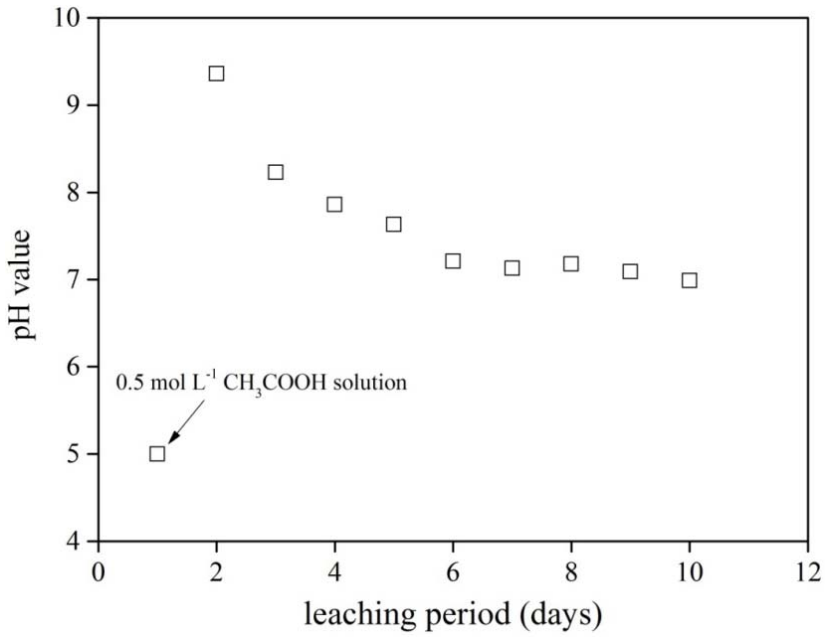

Fig. S3 Final pH value of leaching solutions for different period. 0.5 mol·L^{-1} CH_3COOH is used as leaching solution (sustainable pH of 5) on first day, and subsequently nine successive leaching processes are conducted with a simulated acid rainwater (pH 3.0 ± 0.2).