Supplementary Information (SI)

Geochemical and petrological studies of high sulfur coal and overburden from Makum coalfield (Northeast India) towards understanding and mitigation of acid mine drainage

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1. Lab-scale remediation study of AMD

An experiment for the neutralization of AMD (SE1) was carried out by using limestone collected from Meghalaya, India. The laboratory-based method adopted in this experiment was carried out in a burette. We used a minimum volume of SE1 AMD water for neutralization against a controlled amount of limestone. Limestone of size 3.18 mm was used and the samples were packed in burette (Dimension: length 45 cm, volume 25 ml. Each burette was filled with four different amounts of limestone i.e., 10, 20, 30, and 40 g respectively. The mine water (SE1) of pH 3.1 was poured slowly in an equal amount into the burette and after the treatment, the value of pH, electrical conductivity (EC), and dissolved oxygen (DO) of the treated mine waters were determined. The total amount of limestone, pH, and total time taken, the volumes of mine water needed in each burette for neutralization

along with its flow rate were recorded. The final pH, DO, and EC of mine water from each burette were determined.

2. Prototype based AMD remediation Study

Limestone taken from Meghalaya, India, was used in an experiment for the neutralisation of SE1 AMD water. The four major materials utilised in the filtering process were charcoal, limestone, sand, and water hyacinth. Total 1000 L of SE1 was processed in three stages using the prototype (Fig. 2) produced for the treatment. We performed the functioning of the remediation experiment of a specific amount of SE1 AMD water at a time, that was allowed to pass through all the three stages (S1, S2, S3) developed in the prototype. Specific amounts of SE1 AMD water were designated as R1, R2, R3, R4. The first step was to introduce R1amountof SE1 acid mine water into stage 1 reservoir (S1), which was already filled with water hyacinth *(Eichhorniacrassipes)*, followed by processing using limestone. Three limestone chambers had been erected and linked to the reservoir through corrugated pipes. Four different mesh sizes of limestone (0.296 mm, 0.420 mm, 3.180 mm, and 3.180 mm) were employed, and the samples were placed in four distinct sets of 2 litres columns. 2.4 kg of limestone was used to fill each column. The valves regulate the flow of water between the pipes. The processed water was then treated in the sand chamber in the stage 2 reservoir (S_2). The water that had exited the chamber was then permitted to travel through the stage 3 reservoir i.e., final step, charcoal. As a result, the filtrate product was eventually recovered. Similarly, in this same way we processed a total of 1000 L of SE1 AMD water by running a specific amount at a time and was allowed to pass through all the three stages, present in the protype. The samples collected from each stage were represented as S1R1, S2R1, S3R1 for R1 amount of SE1 acid mine water; S1R2, S2R2, S3R2 for R2 amount of SE1 acid mine water and S1R3, S2R3, S3R3 for R3 amount of SE1 water and S1R4, S2R4, S3R4 for R4 amount of SE1 water, respectively. After treatment, pH of the mine water was determined.

The columns were then filled with fresh limestone. Each column's total amount of limestone utilised for neutralisation was noted. The amounts of mine water required in each column for neutralisation (up to pH 6.5-7) were then gathered, and ultimate pH, TDS, and EC of the mine water was assessed using a pH metre. The same process was repeated in two phase (A and B) by changing the limestone and water hyacinth after one phase was completed. Fig. S2 displays the schematic diagram of the prototype depicting the different steps involved in treating acid mine water.

3. Analytical characterizations

3.1 X-ray photoelectron spectroscopy (XPS)

The nature of the chemical bonding of elements (C, Fe, and sulfur) was determined using an X-Ray photoelectron spectrometer (ESCALAB Xi+). The filtrate received from aqueous leached coal and over burden samples (for 1 hr at room temperature) were coated in a small glass slide (12 mm x 6 mm x 1mm) and kept to dry in a hot air oven (temperature=50^{o}C) to form a thick film before analysis. This analysis was performed to find the impact of pyrite and other ferric ions along with the C-S bond in AMD generation.

3.2 High-resolution transmission electron microscopy (HR-TEM)

High-resolution transmission electron microscopy (HR-TEM) was used to analyze the microstructures of the coal and OB samples. HR-TEM images were acquired on a JEM-2100 Plus electron microscope (JEOL Co., Ltd, Japan) operated at 60–200 kV accelerating voltage. EDS analysis were also carried out by using the x-ray detector associated with the TEM.

3.3 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The elemental concentrations in the mine water as well as the leachates samples were determined by using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (SCIEX Perkin Elmer Elan DRC II (Canada). For this analysis, the liquid samples were digested by preparing aqua regia (1:3= HCl 37%: HNO3 67%) (Islam et al., 2021). Following

digestion, the sample was allowed to cool and filtered into a 25-mL volumetric flask using Whatman filter (No. 1) paper and having the volume further refilled off with deionized water. The samples that had been digested were then put into the device to look for elements including Al, Fe, Pb, Cr, Co, Mn, Zn, Cu, and Ni.

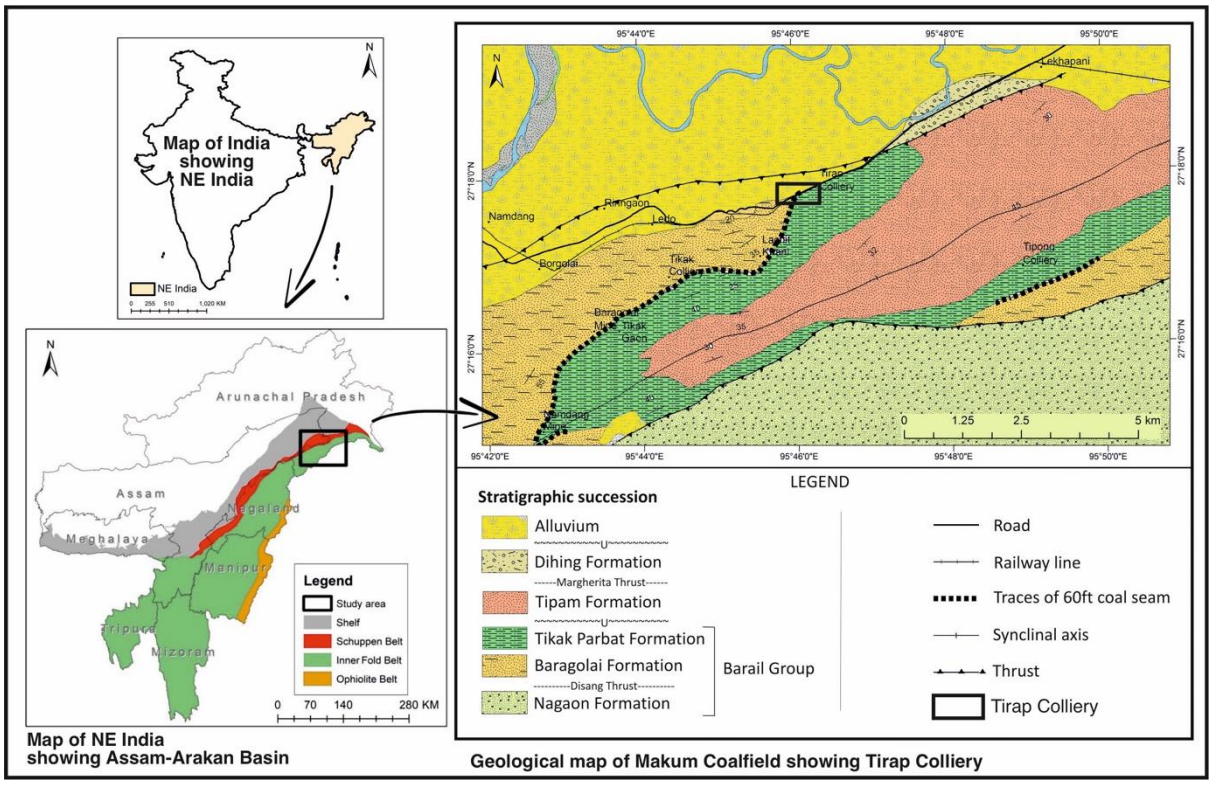

Fig. S1: Location, geological map (modified after Misra, 1992) and stratigraphic succession (modified after Mathur and Evans, 1964) of Makum coalfield.

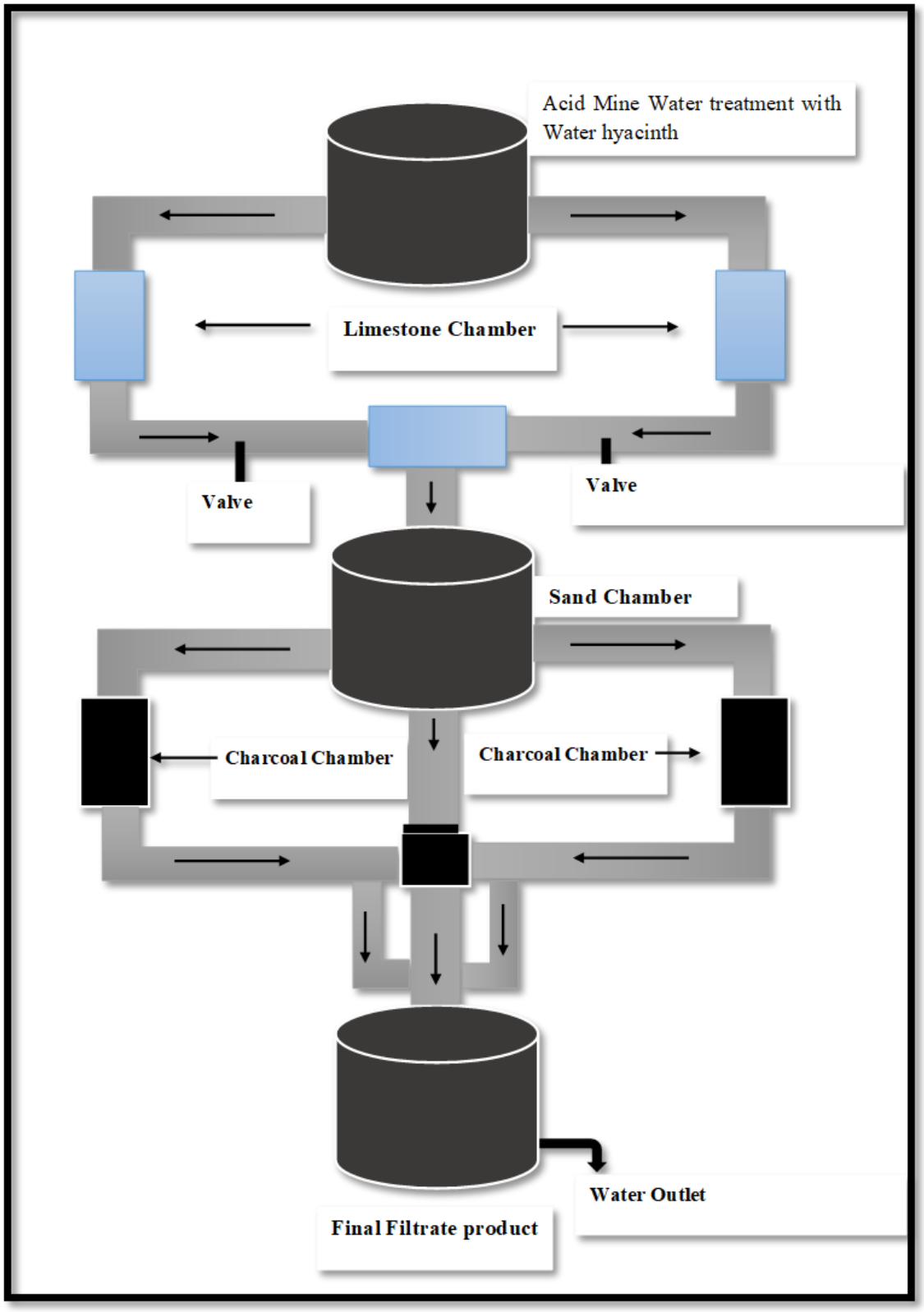

Fig. S2: Schematic diagram of the prototype developed depicting the different steps involved in treating acid mine water (SE1) at pilot plant of CSIR-NEIST.

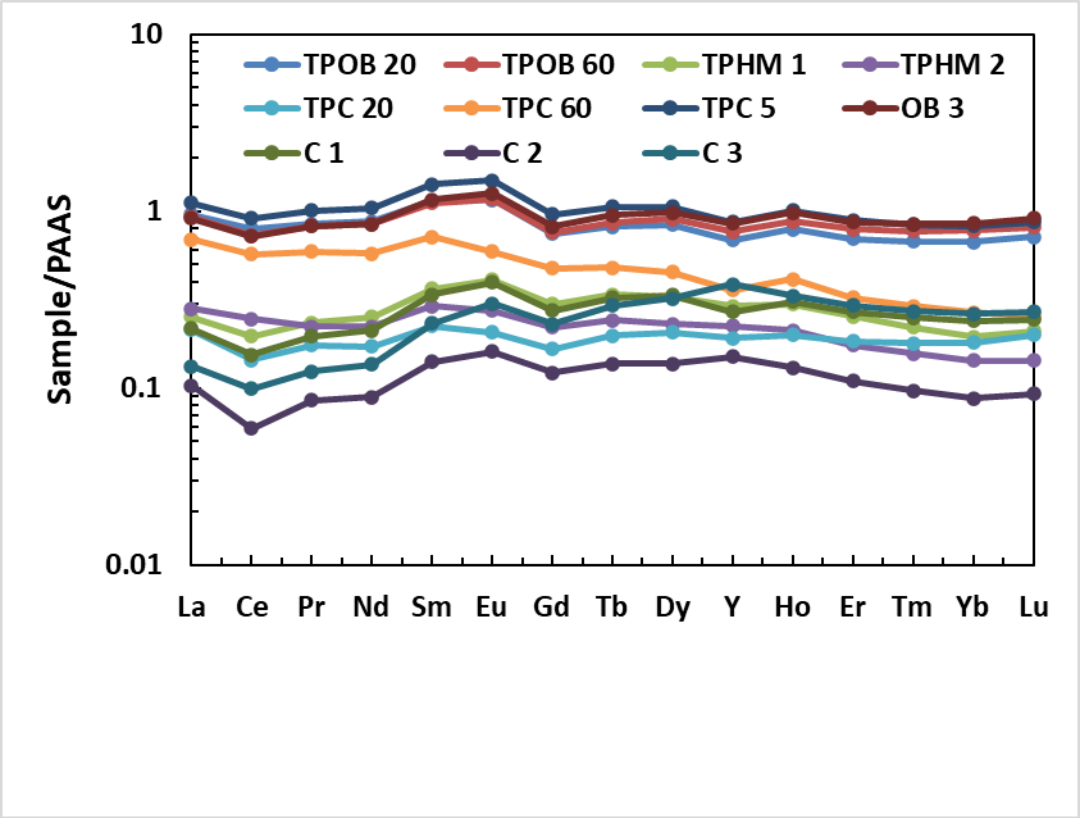

Fig. S3: Post-Archean Australian Shale (PAAS) normalized REY distribution pattern of the samples

Table S1: Sample details and their codes

Sample designation	Sample codes
Raw coal samples collected from Makum coalfield	TPHM1, TPC20, TPC60, TPC5, C1, C2, C3
Raw overburden samples collected from Makum coal fields	TPOB20, TPOB60, OB3
AMD water from Makum coal fields	SE1
Samples after experiment	
Aqueous leachates of coal sample TpC20 (After leaching at different temperature and time regime	TpC-1, TpC-2, TpC-3, TpC-4, TpC-5, TpC-6, TpC-7, TpC-8, TpC-9
Aqueous leachates of overburden sample TpOB20 (After leaching at different temperature and time regime	T_pOB-1, T_pOB-2, T_pOB-3, T_pOB-4, T_pOB-5, T_pOB-6, T_pOB-7, T_pOB-8, T_pOB-9,
Processed AMD water samples after being treated in the prototype station	S1R1, S2R1, S3R1), (S1R2, S2R2, S3R2), (S1R3, S2R3, S3R3) and (S1R4, S2R4, S3R4)

Table S2: Reaction parameters of static aqueous leaching of coal to determine the capacity for AMD generation.

Amount to be taken		Parameters to be changed		Stirring rate (rpm)
Coal sample weight	Volume of H_2O (mL)	Reaction time (mins)	Reaction temperature (^oC)	
20 g	150	30	25	150
		60	45	
		90	90	

Table S3: Maceral composition (vol. %), mineral matter content (vol. %), vitrinite random reflectance of the Tirap colliery representative coal samples.

Maceral	**TpH-M1**	**C3**
Collotelinite	21.2	24.4
Total vitrinite	**21.2**	**24.4**
Sporinite	8	6
Cutinite	13.2	5.2
Suberinite	3.6	5.6
Resinite	10.4	19.2
Exsudatinite	3.6	0.8
Liptodetrinite	5.6	12.8
Total Liptinite	**44.4**	**49.6**
Semifusinite	2.8	2
Funginite	12	2.4
Total Inertinite	**14.8**	**4.4**
Argillaceous matter	11.6	19.2
Pyrite	8	2.4
Total Mineral matter	**19.6**	**21.6**
VRr	**0.50**	**0.51**

Table S4: REYs distribution the samples (in ppm)

	TPOB 20	TPOB 60	TPHM 1	TPHM 2	TPC 20	TPC 60	TPC 5	OB 3	C 1	C 2	C 3
La	36.614	35.314	9.640	10.756	8.145	26.548	42.566	34.778	8.288	3.939	5.068
Ce	63.286	57.987	15.681	19.538	11.436	45.323	72.422	57.559	12.261	4.695	7.890
Pr	7.492	7.304	2.064	1.962	1.549	5.208	8.912	7.293	1.740	0.755	1.093
Nd	29.542	28.562	8.555	7.559	5.824	19.575	35.314	28.625	7.185	3.005	4.601
Sm	6.328	6.198	2.016	1.614	1.247	3.968	7.893	6.465	1.878	0.781	1.285
Eu	1.249	1.259	0.444	0.296	0.223	0.640	1.604	1.360	0.427	0.173	0.325
Gd	3.463	3.522	1.387	1.028	0.776	2.211	4.465	3.819	1.280	0.567	1.076
Tb	0.635	0.665	0.261	0.187	0.153	0.370	0.820	0.733	0.250	0.106	0.228
Dy	3.930	4.230	1.547	1.078	0.968	2.114	4.949	4.608	1.563	0.644	1.498
Y	18.49	20.58	7.84	6.06	5.16	9.68	23.44	23.04	7.26	4.06	10.393
Ho	0.784	0.864	0.296	0.210	0.198	0.407	1.000	0.973	0.305	0.129	0.330
Er	1.996	2.257	0.727	0.500	0.523	0.925	2.531	2.472	0.771	0.313	0.837
Tm	0.273	0.313	0.089	0.063	0.072	0.118	0.340	0.342	0.102	0.039	0.111
Yb	1.892	2.201	0.551	0.404	0.510	0.756	2.317	2.396	0.677	0.246	0.740
Lu	0.310	0.351	0.091	0.062	0.087	0.110	0.376	0.394	0.105	0.040	0.117

Table S5: Normalising Values of PAAS

	PAAS
La	38.2
Ce	79.6
Pr	8.83
Nd	33.9
Sm	5.55
Eu	1.08
Gd	4.66
Tb	0.774
Dy	4.68
Y	27
Ho	0.991
Er	2.85
Tm	0.405
Yb	2.82
Lu	0.433
	211.77

Table S6: Post-Archean Australian Shale (PAAS) normalized values

TPOB 20	TPOB 60	TPHM 1	TPHM 2	TPC 20	TPC 60	TPC 5	OB 3	C 1	C 2	C 3
0.9584874	0.924456	0.252358	0.281561	0.2132137	0.6949615	1.1142898	0.910409517	0.216975515	0.10311096	0.132675124
0.7950504	0.728484	0.196995	0.245446	0.1436686	0.5693898	0.9098299	0.723101292	0.154038002	0.05897743	0.099119585
0.8484219	0.82719	0.233755	0.22224	0.1754056	0.589852	1.0092418	0.825945814	0.197018835	0.08549793	0.123811622
0.8714503	0.842537	0.252373	0.22298	0.1717991	0.5774212	1.0417139	0.8444013	0.211949908	0.08863471	0.135720738
1.1401508	1.116792	0.363274	0.290889	0.224758	0.7149984	1.4221462	1.164953359	0.338379864	0.14068297	0.231595331
1.1563186	1.166023	0.410694	0.27381	0.2064933	0.5926187	1.4855687	1.259157543	0.39570908	0.16045912	0.300953956
0.7431454	0.755828	0.297675	0.220564	0.1665345	0.4744507	0.9581758	0.819620888	0.27463817	0.12172973	0.230965826
0.819787	0.858585	0.33669	0.241307	0.1977062	0.4780987	1.0588331	0.947300792	0.322800994	0.1371283	0.294343099
0.8397773	0.903931	0.330541	0.230316	0.2068898	0.4517244	1.0575212	0.984585134	0.333876433	0.13762429	0.320028882
0.6849621	0.762318	0.290497	0.224306	0.1911734	0.3584351	0.8681933	0.853157707	0.268779246	0.15020955	0.384925926
0.7910115	0.872078	0.298732	0.211758	0.1998671	0.4111189	1.009396	0.981616457	0.307970023	0.13014575	0.332540198
0.7004105	0.792088	0.255197	0.175431	0.1833427	0.3247103	0.8880995	0.867432887	0.270654595	0.1098825	0.293518719
0.6736215	0.772526	0.220985	0.156434	0.1789646	0.2908743	0.8396061	0.843580517	0.250677716	0.09669981	0.272944072
0.6709564	0.78036	0.195303	0.14335	0.1809294	0.2679944	0.8215466	0.849704085	0.239920521	0.08720624	0.262379554
0.7159258	0.810511	0.210802	0.143253	0.2001013	0.254944	0.8689761	0.910718328	0.243306601	0.09309378	0.270193133

Table S7: Comparison of important ratios studied samples with mafic, felsic, UCC and PAAS ratios (Nagarajan et al., 2007 and references therein)

Important Elemental ratios	**Range of Samples Under Present Study**		**Range of Sediments**		**Upper Continental Crust**	**Post-Archaean Australian Average shale**
	Coal Samples	**Other Samples**	**Felsic rocks**	**Mafic rocks**		
Th/Sc	0.08-0.425	0.35-1.33	0.84-20.5	0.05-0.22	0.79	0.9
Th/Co	0.009-0.115	0.11-0.62	0.67-19.4	0.04-1.4	0.63	0.63
Th/Cr	0.009-0.027	0.017-0.007	0.13-2.7	0.018-0.046	0.13	0.13
Cr/Th	37.2-233.9	13.2-60.06	4.00-15	25-500	7.76	7.53
La/Sc	1.00-1.5	1.8-7.5	2.5-16.3	0.43-0.86	2.21	2.4

Table S8: Variation of Pyritic Sulfur (wt %) with temperature and time of leaching of Tirap coal and overburden (OB) sample.

Samples	TpC			TpOB		
Time of stirring (rpm)	25^{o}C	45^{o}C	90^{o}C	25^{o}C	45^{o}C	90^{o}C
0	0.52	0.52	0.52	0.86	0.86	0.86
30	0.437	0.419	0.401	0.586	0.534	0.501
60	0.338	0.314	0.305	0.372	0.343	0.294
90	0.275	0.254	0.229	0.269	0.223	0.184
Over night	0.245	0.222	0.211	0.221	0.189	0.156

Table S9: Burette-based AMD treatment utilising Meghalaya Limestone

Amount of limestone taken (g)	pH (Initial- final)	Total Time Taken (mins)	Total water added (ml)	Flow rate (avg.) ml/sec
10	6.6-6.3	6	20	0.056
20	6.8-6.4	12	20	0.027
30	7.0-6.5	16	20	0.021
40	7.0-6.6	21	20	0.016

Table S10: Results of Burette-based AMD treatment

Amount of limestone taken (g)	pH (final)	EC (mS/cm)	DO (mg/L)
10	6.3	5.63	4.59
20	6.4	5.26	4.28
30	6.5	4.98	4.47
40	6.6	4.71	4.30

Table S11: Table displaying pH variations following treatment in the prototype station

Phase A (Before changing of water hyacinth)			
Batch	Time(min)	pH	Volume of Water(L)
	48	6.2	110
	32	6.5	80
	32	6.5	80
	32	5.5	80
1st Batch	32	6.1	80
Phase B (after changing of water hyacinth)			
	33	6.4	80
	34	6.5	80
	32	6.3	80
	32	6.4	80
2nd Batch	29	6.7	50
	22	6.3	50
	21	6.4	50
	21	6.3	50
3^{rd}Batch	22	6.4	50

Table S12: ICP-OES elemental concentrations of Phase-A treatment of the AMD

	S1R1-A	S2R1-A	S3R1-A	S1R2-A	S2R2-A	S3R2-A	S1R3-A	S2R3-A	S3R3-A	S1R4-A	S2R4-A	S3R4-A
Al	5.67	0.223	0.129	4.75	1.89	0.112	5.07	0.318	0.105	5.31	4.63	2.13
B	0.06	0.065	Bdl	0.068	0.07	0.045	0.048	0.056	0.057	0.033	0.059	0.064
Ba	0.051	0.104	0.006	0.04	0.071	0.081	0.048	0.041	0.066	0.05	0.047	0.07
Ca	240	323	1.03	260	287	309	220	322	293	215	238	269
Cd	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Co	0.343	0.266	0.005	0.35	0.371	0.208	0.329	0.279	0.193	0.323	0.336	0.303
Cr	0.019	0.019	0.003	0.022	0.024	0.013	0.017	0.017	0.013	0.017	0.018	0.026
Cu	0.075	0.012	0.006	0.041	0.029	0.002	0.029	0.004	0.003	0.035	0.033	0.019
Fe	3.58	0.132	0.078	0.54	0.164	0.033	2.68	0.169	0.091	3.01	0.809	0.146
Mg	564	524	2	571	574	518	527	537	535	526	540	547
Ni	2.21	1.38	0.017	2.2	2.11	1.16	2.03	1.57	1.32	2.05	2.06	1.81
Pb	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Zn	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl

Table S13: ICP-OES elemental concentrations of Phase -B treatment of the AMD

	S1R1-B	S2R1-B	S3R1-B	S1R2-B	S2R2-B	S3R2-B	S1R3-B	S2R3-B	S3R3-B	S1R4-B	S2R4-B	S3R4-B
Al	5.02	4.01	0.08	5.35	0.12	0.082	6.26	4.74	0.171	6.35	4.75	0.127
B	0.068	0.072	0.066	0.06	0.065	0.063	0.06	0.078	0.092	0.071	0.08	0.075
Ba	0.086	0.099	0.07	0.088	0.084	0.042	0.066	0.067	0.058	0.067	0.068	0.056
Ca	280	311	306	262	293	335	276	296	352	287	303	322
Cd	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Co	0.398	0.4	0.199	0.377	0.35	0.07	0.408	0.389	0.297	0.426	0.406	0.275
Cr	0.014	0.021	0.021	0.017	0.022	0.012	0.017	0.013	0.016	0.023	0.021	0.024
Cu	0.013	0.019	0	0.005	0	Bdl	0.023	0.016	0.003	0.025	0.017	0.001
Fe	0.569	0.124	0.006	0.915	Bdl	Bdl	0.025	0.066	Bdl	0.08	0.07	Bdl
Mg	615	647	589	598	603	619	620	615	632	622	619	613
Ni	2.36	2.46	1.45	2.24	2.13	0.996	2.49	2.42	1.89	2.56	2.44	1.75
Pb	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
Zn	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl

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