The Use of Industrial Alkaline Wastes to Neutralise Acid Drain Water from Waste Rock Piles

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Abstract

Coal mining always results the formation of large volumes of rock wastes, which can be stacked in piles. Around 100 piles of various sizes are located in the Kizel coal basin, Western Urals, Russian Federation; some of these piles are burned nowadays. Rock piles drainage water have pH – 1,8-6,3, Fe – 0,2-28050 mg L⁻¹, Al – 0,5-3550 mg L⁻¹, Mn – 0,13-88 mg L⁻¹, and total mineralization – up to 50000 mg L⁻¹. A lot of metals and metalloids are transported with drain water from waste piles to soil, groundwater and the nearest river systems and pollute them.

We studied the capability of industrial alkaline wastes, covered waste rock piles, to neutralise drain water, formed during rainfalls. Preliminary laboratory experiments showed high efficiency of acid mine water treatment with lime-containing metallurgical slag, alkaline soda plant's waste and limestone mining waste. The last two substances were used as reagents in the burned and unburned waste rock piles treatment experiment. Two solutions were separately used as leaching agents – distilled water to mimic rainfalls, and solution of organic substances (glucose and sodium acetate, 0.5 g L^{-1} each) to mimic rainfalls, drained plant vegetation.

The most effective alkaline reagent for drain water neutralization was soda plant's waste. The investigation revealed that organic substances addition increased the efficiency of waste rock piles treatment with alkaline wastes used. Mathematical calculations showed that covering of waste pile with 0.3 m thick layer of soda plant's waste could be enough for long term neutralization of drain water, being formed during rainfalls.

The using of alkaline industrial byproducts and wastes to cover waste rock piles could be economically appropriated treatment method in the Kizel coal basin because such wastes are located in transport accessibility with the basin. The efficiency of alkaline reagents using could be improved by organic matter addition.

Keywords: Waste Rock Pile, Acid Rock Drainage, Industrial Alkaline Wastes, Column Leaching Experiment

Introduction

Mining industry is associated with the production of large quantities of waste, which potentially may cause environmental problems over very long periods of time. The primary process that causes problems is the oxidation of the sulfide minerals in the waste, which are deposited as waste piles or tailings.

Mining in the Kizel coal basin had been carried out for more than 200 years. Mines were closured in the 1990s. Over 35 million m³ of waste rocks had been accumulated in more than 100 piles, composed of fragments

of argillite, sandstone, and limestone with inclusions of coal; the content of pyrite in piles reaches 4%. Processes of physical weathering, oxidation, hydrolysis, hydration, and metasomatism occur within piles. The oxidation of pyrite releases sulfur acid and is accompanied with heat production. So, selfignition and burning of piles, roasting and melting of their rocks, and fumarole processes within piles were detected. Rainfalls, drained piles, are enriched in soluble compounds and pollute soils, groundwaters and rivers (Khayrulina *et al.* 2016).

To prevent the pollution and acidification of natural waters from mining waste leachates, it is necessary to minimize sulfide oxidation and/or water infiltration in the waste deposit. The installation of unpermeable or semi-permeable covers, the growth of vegetation, the addition of acidbuffering materials are used to prevent formation of acid rock drainage. As the pH of the leachate is of critical importance for the discharge of contaminants, because the solubility and mobility of metals and semimetals critically depend on their speciation, the use of carbonate minerals and carbonatecontaining waste as the cover to waste pile could be an appropriate measure to prevent environment pollution.

The aim of this study is to investigate the capability of carbonate-containing wastes to neutralize the leachate of waste rock piles in small-scale column experiment.

Materials and Methods

Site Description and Sampling

The Kizel coal basin (the Western Urals, Russia) occupies area of 200 km² and is located within West Urals folding zone adjacent to the pre-Ural boundary deflection. Rocks of Palaeozoic (Middle Devonian -Late Permian) age are developed in the area and represented by sandstones, mudstones, siltstones, shales, limestones, dolomites, marls, coals, and others. Carbonate rocks are intensely karsted, especially in the upper part of geologic column. Quaternary deposits are mainly represented by sands, loams, and clays and have often a high content of gravel and pebbles (Khayrulina et al. 2016). Coal of the basin exhibits elevated content of sulfur (mainly as a pyrite) - 5.8% (Kler 1988). Annual average regional precipitation is 800-900 mm/a, and the annual average of air temperature is 0-2 °C, with 160-170 days with an average air temperature below 0 °C (Maksimovich, Pyankov 2018).

Samples of burned and unburned waste rocks were taken from the partially burned pile of "Severnaya" mine. About 10 kg of rocks were separately sampled at burned and unburned parts of the pile from the depth of 0.5 m below pile surface. The moisture content of burned waste rock was 18%, pH of water suspension was 3.8. The moisture content of unburned waste rock was 14%, pH of water suspension was 2.8. Samples were sieved and the fraction of less than 1 mm in dimensions was used in column leaching experiment.

Alkaline Wastes

Carbonate-containing wastes of two industrial enterprises, soda plant in Berezniki town and limestone mining quarry at Chusovoy town, were used as alkaline reagents in experiment. These enterprises are located in the transport accessibility with the Kizel coal basin – 20 km for limestone quarry, and 120 km for soda plant.

Soda plant's waste was sampled from the tailing dump. It comprised the water suspension of various minerals with liquid:solid ratio of 85:15 and pH 9.5. Total mineralization of liquid phase was about 180 g L⁻¹ (Maksimovich, Pyankov 2018). To determine the water content, the subsample was weighted before and after drying for 2 days at 60 °C. Water content of soda plant's waste was 88%. Mineral composition of the solid phase is presented in tab. 1.

Sample of crushing waste was taken from limestone mining quarry and sieved. The fraction of less than 1 mm in dimensions was used in column leaching experiment. To determine the water content, the subsample was weighted before and after drying for 2 days at 60 °C. Bulk density of the sample was 1.53 kg m⁻³, water content – 2%. Mineral composition of the sample is presented in tab. 1.

Table 1 Mineral characteristics of alkaline wastes, %.

Mineral	Soda plant's waste	Limestone mining waste		
Calcite	90.6	88.7		
Dolomite	0.6	2.4		
Quartz	0	8.9		
Cristobalite	0.4	0		
Gypsum	4.3	0		
Halite	4.1	0		
Total	100	100		

Alkaline reagent	Soda plant's waste		Limestone mining waste			No reagents		
Amount of alkaline reagent, %	1	5		1	5			
Leaching solution ^a	W	w	S	w	W	S	w	S
Burned waste rock pile	2, 3	5, 6	4	8, 9	11, 12	10	7	1
Unburned waste rock pile	14, 15	17, 18	16	20, 21	23, 24	22	19	13

Table 2 The numeration of columns in the leaching experiment.

 $^{\rm a}$ W – distilled water, S – solution of glucose and sodium acetate, 0.5 g $\rm L^{\text{-1}}$ each.

Column Leaching Experiment

Inverted bottom-cutted 0.5 L bottles made of high density polyethylene (HDPE) were used as cylindrical columns with tapered lower part. The dimensions of cylindrical part were 0.09 m in height and 0.06 m in diameter. The height of conical part was 0.12 m, diameters of conical part were 0.06 and 0.025 m. The lower end of inverted bottle (bottle neck) was sealed with the cap with glued rubber tube (0.2 m in length, 0.005 m inner diameter). HDPE grid (average pore size of 0,5 mm) and filter paper were placed inside the cap to hold sample and prevent finer sample particles escaping from column. Assembled columns were acid washed, triple rinsed with deionised water, and air-dried before use.

250-270 g of waste rock sample was placed into the column and covered evenly with an alkaline reagent, then 50-70 ml of a leaching solution was carefully added to the top of the column to avoid the erosion of cover layer. After percolation of the solution through the column, formed leachate was collected in glass jars and its pH was estimated. The addition of the solution was once a day, the channeling and preferential routs were not observed in the columns during experiment. Columns leaching experiment was performed at room temperature (22.5 \pm 2.5 °C), the evolution of the leachate's pH was examined.

Different amounts of alkaline reagents were used to cover waste rock samples, 1 and 5% wet weight of waste rock wet weight. Control columns did not contain alkaline reagents.

Two solutions were separately used as leaching agents – distilled water to mimic rainfalls, and solution of organic substances (glucose and sodium acetate, 0.5 g L^{-1} each)

to mimic rainfalls, drained plant vegetation. The matter is, the most of piles are covered with vegetation, so percolating rainfalls are enriched in organic matter originated from root exudates and decomposed plant residues. As a removal of vegetation before the alkaline treatment of piles could be costly and technically difficult, it was the reason to use the solution of organic substances in the experiment. The experiment's scheme is presented in tab. 2.

Results and Discussion

Results of the column experiment with different leaching solutions are presented in fig. 1. Initial pH of water suspensions of burned and unburned waste rock samples were 3.8 and 2.8, correspondingly. pH of distilled water, percolated through the columns, had a tendency to rise gradually and reached 4.4 and 3.5 at 84th day of the experiment. This effect could be attributed to the presence of such alkaline-generating minerals in waste rock piles, as limestone. The presence of this mineral in waste rock piles was observed (Khayrulina *et al.* 2016).

Addition of organic substances to water, percolated through the columns, induced more substantial rise of pH: *approx*. 5.1 to both burned and unburned waste rock samples at 44th day of the experiment, and *approx*. 6.1 and 5.4 at 84th day, correspondingly. These organic substances, glucose and sodium acetate, are readily used by bacteria, inhabiting pile's rocks and producing CO_2 as an end-product in metabolic processes. We supposed, the implementation of plants vegetation on the pile's surface could to some extent be an acid drainage prevention





- *a) burned and unburned waste rock + soda plant's waste, 5% + water;*
- *b)* burned and unburned waste rock + soda plant's waste, 1% + water;
- *c) burned and unburned waste rock + limestone mining waste, 5% + water;*



d) *burned and unburned waste rock* + *limestone mining waste, 1%* + *water;*

e) burned waste rock: column 4: + soda plant's waste, 5% + Corg solution; column 10: + limestone mining waste, 5% + Corg solution; column 1: + Corg solution; column 7: + water;

f) unburned waste rock: column 16: + soda plant's waste, 5% + Corg solution; column 22: + limestone mining waste, 5% + Corg solution; column 13: + Corg solution; column 19: + water.

measure due to enhanced water transpiration by plants, decreasing the amount of drained water, and addition of organic substances, originating from living and dead plants and inducing both bacterial metabolism and formation of CO_2 in piles.

The covering of waste rock samples with alkaline reagents rose pH of leaching solutions. The effect of soda plant's waste addition did not substantially differ from limestone mining waste addition, as it can be seen in fig. 1. However, the water content was 88% in soda plant's waste, whereas it was 2% only in limestone mining waste. So, soda plant's waste was the most effective alkaline reagent in the experiment, based on dry weight calculation.

The highest pH values were observed in columns covered with alkaline reagent and drained with solution of organic substances.

Mathematical calculations showed that covering of waste pile with 0.3 m thick layer of soda plant's waste could be enough for long term neutralization of drain water, being formed during rainfalls.

Conclusions

The using of alkaline industrial byproducts and wastes to cover waste rock piles could be economically appropriated treatment method in the Kizel coal basin because such wastes are located in transport accessibility with the basin. The efficiency of alkaline reagents using could be improved by organic matter addition.

Acknowledgements

The reported study was funded by RFBR, project number 19-05-50073.

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