## Use of alkaline waste products for acid mine water purification

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**Abstract:** The recent cessation of mining in the Kizel Coal Basin has caused serious environmental problems for the Western Urals area, Russia. After mine closure, acid minewaters (pH about 3) began to pollute the ground surface and rivers. Within the last five years, the tributaries of the Kama and Chusovaya Rivers have become highly polluted with dissolved metals. The methodology for the neutralization of acid mine water by alkaline waste products is discussed in the paper. The waste products are from the Bereznikovsky Soda Factory and are non-toxic consisting of 70-80% calcite (CaCO<sub>3</sub>). These waste products are capable of neutralizing mine water causing the precipitation of iron, aluminium and heavy metals, and acceptable dissolved concentrations in the stream water.

**Résumé:** Le cessation récent à moi dans le bassin de charbon de Kizel a posé des problèmes écologiques sérieux pour la région occidentale des Monts Oural, Russie. Après la fermeture de mine, la mine acide arrose (le pH environ 3) a commencé à polluer la surface et les fleuves moulus. Dans les cinq dernières années, les tributaires des fleuves de Kama et de Chusovaya sont devenus fortement pollués avec les métaux dissous. La méthodologie pour la neutralisation de l'eau acide de mine par les déchets alkalins est discutée dans le papier. Les déchets sont de l'usine de soude de Bereznikovsky et sont la calcite 70-80% se composante non-toxique (CaCO3). Ces déchets sont capables de neutraliser l'eau de mine causant la précipitation du fer, de l'aluminium et des métaux lourds, et les concentrations dissoutes acceptables dans le jet arrosent.

Keywords: geochemistry, ground contamination, remediation, surface water

#### INTRODUCTION

The geology in the Kizel Coal Basin, West Urals, Russia, is largely Carboniferous and the recent cessation of mining in the area and subsequent water table rebound have caused serious environmental problems. After mine closure, geochemical interaction between acid minewaters and the surrounding geology has resulted in high concentrations of iron, aluminium and trace metals in the tributaries of the Kama and Chusovaya rivers. The coal horizons in the Kizel Coal Basin differ from other basins in the region as they contain high levels of sulphur (mainly as a pyrite) (5.8%) and ash (21.5%) (Kler et al. 1988) (Figure 1).

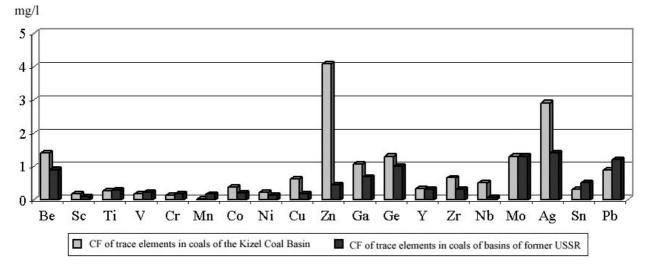


Figure 1. Coefficient factors (CF) of trace elements in coals of the Kizel Coal Basin and coals of basins of former USSR (Kler at al. 1988)

#### **MINEWATER CHEMISTRY**

The mine water chemistry is largely dependent on the levels of sulphur, carbonate and trace element found within the carboniferous strata. A concentration of more than 4% pyrite results in acid water (pH=2-3) and a sulfide chemistry. Total Dissolved Solid (TDS) concentrations of the sulfide (Fe-Al, Na-Ca) waters of the Kizel Coal Basin

was 2.5-19 g/l and levels higher than this were reached during exploitation. Lead, copper, zinc, silver, nickel and cobalt content and other trace elements in the acid mine water are elevated in comparison with natural growndwater (Maximovich, Gorbunova 1990).

During exploitation of the basin, minewaters were released to the surface without any prior purification or treatment. Before mine waters entered the river network, natural levels of the hydrochemical facies  $HCO_3$ -Ca-Na (TDS of 90-150 mg/l) were circum-neutral.

Before entering of mine waters, small rivers had  $HCO_3$ -Ca-Na hydrochemical facies (TDS of 90-150 mg/l) and were circum-neutral. After entering of mine waters, they were characterized by  $SO_4$ -Fe-Al chemistry with TDS ranging from 640 to 6000 mg/l, sulphate concentration - from 1000 to 3700, iron - 70 - 900, aluminium - 11 - 160 mg/l at pH 2.5-2.9 (Maximovich, Kataev & Blinov 1995)

Mine closure occurred during the 1990s but this did not resolve the environmental problems. Despite acid mine waters no longer being pumped to the surface, 12 disused mine adits started to discharge water to the surface once groundwater rose to its natural level (Figure 2).



Figure 2. Discharge area to the River Kos'va

## **RIVER WATER POLLUTION**

The total average annual flow for the River Kos'va is  $2500 \text{ m}^3$ /hour. This is several times less than during mining activity. However, the TDS of discharge increased greatly – up to and in excess of 25 g/l (Figure 3). The ferrous iron content increased sharply - up to 5 g/l. Discharge waters entered 19 rivers, 15 of which are sourced for water use.

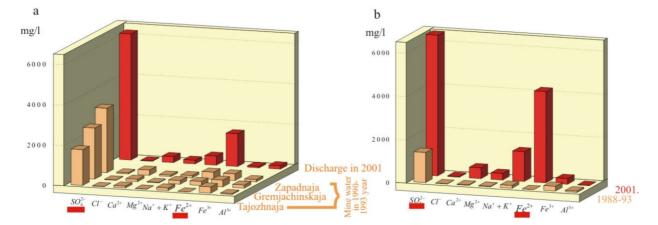


Figure 3. Chemistry of mine water before and after mine closure (a) mines of the city of Gremjachinsk , (b) Kalinin mine

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In the more polluted river sections, accumulations of several tones of man-made bottom deposits have been found. These accumulations include amorphous iron and aluminium hydroxides with high concentration of Mn, Cu, Ni, Zn, Pb and others. These bottom deposits are washed downstream to the Kama and the Chusovaya Rivers, where they become a secondary source of water pollution.

Since the 1980s, the author has actively worked on the problem of purification of acid mine water and spoil heap drainage with the aim to find a method of removing harmful elements using artificial geochemical barriers with industrial waste as a reagent. This research is based on the theory developed by A.I. Perelman and others (Perelman & Kasimov 1999, Emelyanov 2005, Langer 2001, Maximovich, Osovetskiy & Blinov 2000, Sergeev et al. 1996, Nuttal, & Younger 2000, Mclean et al. 2005).

#### REMEDIATION

At the end of the 1980s, alkaline waste products (so-called "white seas") from the Bereznikovsky Soda Factory were tested as a reagent for neutralization of acid discharges. The neutralization technique was developed by Maximovich, Holostov & Basov (2000) (Figure 4). Alkaline waste products consist of 70-80% calcite (CaCO<sub>3</sub>) with pH of 9-12. The average contents of 38 determined elements do not exceed maximum permissible concentration (MPC) in soils (Table 1). Harmful organic compounds were not revealed. The volume of waste, that is ready for using as a reagent for neutralization of acid mine water without any treatment is more then 1 million  $m^3$ .

Table 1. Average data for the alkaline waste products from the Bereznikovsky Soda Factory, mg/kg

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N of sample	Depth, m	pН	Ni	Со	Cr	Mn	v	Sc	Ye	Cu	Zn	Pb	Ba	Sr		Zr	Y	L a	Li	Nb	
1	0		7	3	10	500	10	3	-	20	70	10	5	500	-	50	20	1	15	-	
3	0	8.8	10	5	30	700	10	-	-	15	50	4	200	500	<1	30	40	-	-	-	
2	1.6	11.8	9	4	30	500	10	3	-	18	-	7	300	400	1	30	30	-	-	7	
5	0	8.7	7	3	18	1000	10	3	-	15	-	7	200	400	-	20	40	-	-	-	
4	1.0	11.8	6	3	15	400	10	-	-	10	-	30	200	300	1.5	20	30	-	-	7	
8	0	9.9	6	3	30	700	10	-	-	10	-	7	200	300	1	20	40	-	-	-	
7	1.0	11.4	9	3	30	700	10	-	-	10	-	70	200	300	1	50	40	-	-	-	
6	3.5	11.8	10	3	40	1500	10	3	-	20	50	180	200	400	1	20	40	-	-	7	
11	0	9.2	7	3	30	1000	10	-	-	10	-	20	200	300	-	20	40	-	-	-	
10	1.5	11.5	9	3	50	1000	10	3	-	20	-	180	200	300	15	20	50	-	-	-	
9	4.0	11.6	9	3	70	1000	10	4	-	18	-	180	1500	500	1	30	50	-	-	-	
12	0	12.3	5	-	15	1000	10	3	-	18	-	15	200	200	1	20	15	ŀ	-	-	
13	2.5	124	7	3	30	700	10	3	1	18	-	100	200	200	15	40	18	-	-	-	
14	3.5-	124	9	3	30	900	10	3	-	20	50	150	200	300	1	40	18	-	-	-	
MPC			50	50	100	1500	150			55	100	32									

When acid discharge is in contact with alkaline waste pH increases due to reaction with carbonate and hydroxide of calcium. This leads to a decrease in concentrations of Fe, Al, Mn, Co, Zn, Cu, Ni, Pb, Cd, Ti and other elements resulting in the purification of water.

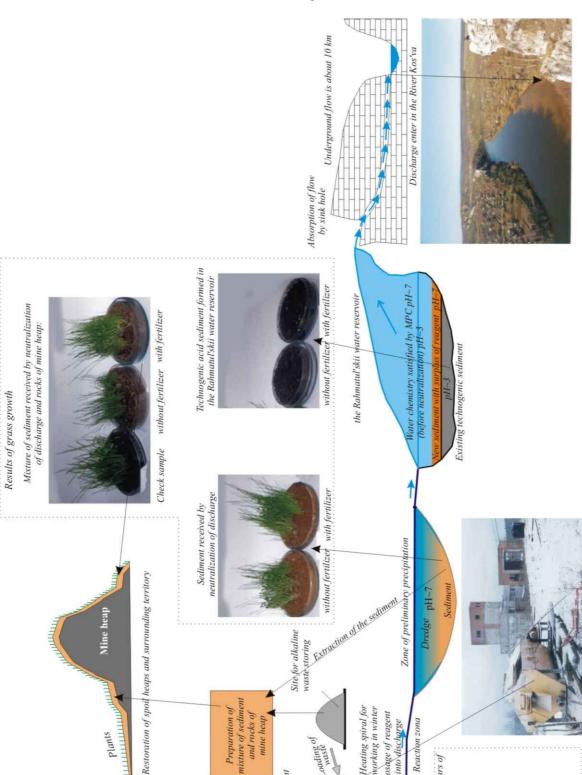
A pilot field experiment was conducted on "The 40 years of October" adit, where discharges of water are from 180-220 m<sup>3</sup>/hour in summer to 300-400 m<sup>3</sup>/hour during flood. Mineralization ranges from 4000-600 mg/l to 800-900 mg/l with pH of 2.6-2.9. Concentrations of some elements exceed MPC: Fe – in 400 times, Al – 46, SO<sub>4</sub><sup>2–</sup>1.3, Be– 52.8, Mn– 36.9, Ni – 2.5, Cd – 1.9, Co – 1.6, Ba – 1.5 and Ti – in 1.2 times.

This experiment showed that the pH of the discharge increased from 2.6-2.9 to 7 resulting in a decrease in the concentration of iron from 30-40 mg/l to 0.2-0.3 mg/l. The content of Al, Be, Li, Ni, Cd, Co and Ti do not exceed MPC (Figure 5).

As a result of neutralization, the sediment becomes a mixture of iron and gypsum hydroxide and carbonate calcium with a neutral pH. Mobile forms of Fe, Al, Mn, Pb and others were not revealed (Table 2). Sediment is overgrowing with perennial grass (timothy, fescue, couch-grass, lucerne) in the same way as the control template of soil.

### CONCLUSION

The pilot field experiment showed the prospect of use geochemical barriers for solving environmental problems. Additionally, this mine water purification technology helps to resolve the serious problem of the disposal of alkaline waste products.



Mine hea

TITITI IIII

plants

Sink

Figure 4. Technological schema of improving of the environment the Kizel Coal Basin by alkaline waste products from the Bereznikovsky Soda Factory

mixture of sediment and rocks of

mine heap

Mixer of reagent preparation

Preparation of

Heating spiral for working in winter

8

Loading of

Delivery of mine water to mixer

Dosage of reagent

into\discharge

Reaction

Dump.

pH~2,8

arge of "The 40 years of

Disch

October" adit excess of MPC

(in times). Fe 390 Al 46 Be 52,8 Mn 36,9 Li 3,5 Ni 2,5 Co 1,6 Ba 1,5

10 MI

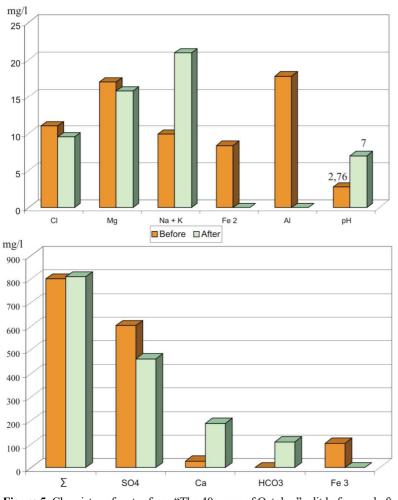


Figure 5. Chemistry of water from "The 40 years of October" adit before and after neutralization of discharges

Sample	рН	Ni	Со	Cr	Mn	V	Sc	Cu	Zn	Pb	Ag	Мо	Ва	Sr	Be	Zr	Y	Nb
	Total content																	
1 (before)	2,92	30	9	150	100	150	1,5	100	100	30	0,2	2	30 0	15 0	10	300	60	30
2 (after)	7,22	70	30	90	1500	40	9	100	500	90	0,2	3	30 0	18 0	10	100	90	15
	Не оπр	40	18	100	1000	30	7	90	400	90	0,1	1,5	30 0	15 0	9	100	70	10
MPC		50	50	100	1500	150		55	100	32								
	Mobile forms																	
1 (before)	2,92	0,81	0,81	0,08	27,1	0,03	0,02	27,1	27,1	0,04	-	0,005	0,8	0,8	0,108	0,14	0,4	0,03
2 (after)	7,22	0,02	-	<0,06	-	<0,06	-	<0,06	0,3	-	-	0,009	1,8	0,6	0,006	0,24	<0,06	0,05

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## REFERENCES

EMELYANOV, E.M. 2005. The barrier zones in the ocean. Springer.

- KLER, V.R., NEHANOVA, V.F. & SOPRYKIN, F.YA. et al. 1988. *Metallogeny and geochemistry of coal-bearing and slate series in USSR*. Nauka, Moscow. (in Russian)
- LANGER, M. 2001. The role of geological barrier in waste disposal projects. In: Proceedings International Symposium on Engineering Geology and the Environment, Athens, Greece, 23-27 June 1997, 4, 617-635. A.A. Balkema, Rotterdam.
- MAXIMOVICH, N.G. & GORBUNOVA, K.A. 1990. Geochemical aspects of the geological medium changes in coal fields. *In:* Proceedings of the 6<sup>th</sup> Congress of the International Association of Engineering Geology. A.A.Balkema, Rotterdam, 1457-1461.
- MAXIMOVICH, N.G., KATAEV, V.N. & BLINOV, S.M. 1995. Consequence of the Kizel Koalfield acid mine water disposal into karst cavities In: Proceeding of the 8th International Symposium on Water-Rock Interaction-WRI-8. Vladivostok, 885-888.
- MAXIMOVICH, N.G., OSOVETSKIY, B.M. & BLINOV S.M. 2000. Geochemical Barriers and Environment Protection. In: GeoEng 2000: Conference Proceedings. 19-24 November 2000. Melbourne, Australia.
- NUTTAL C.A. & YOUNGER P.L. Assessment and experimental passive treatment of zinc-rich net alkaline minewaters, Nent Valley, UK. 2000. In: Mine water and the Environment: Proceedings of 7<sup>th</sup> International Minewater Association Congress, Katowice – Ustron, Poland, 11 – 15 September, 2000. Katowice, 456-463.
- MCLEAN, M., FRIZZELL, J., COATES, R., WRIGHT, Y., WOLF, S. & BRAKE, S. 2005. Effects of crushed limestone application on plant uptake of trace elements in an acidic seep. *In: Salt Lake City Annual Meeting, October 16-19, 2005.*

PERELMAN, A.I. & KASIMOV N.S. 1999. Landscape geochemistry. Astrja-2000, Moscow. (in Russian)

SERGEEV V.I., SHIMKO T.G., KULESHOVA M.L. & MAXIMOVICH N.G. 1996. Groundwater protection against pollution by heavy metals at waste disposal sites. *Water Science Technology*, 34 (7-8), 383-387.