SHUNGITE INFLUENCE ON THE WATER CHEMISTRY

A. Z. Zaidenberg
Institute of Geology, Karelian Research Center,
Russian Academy of Sciences,
Petrozavodsk, Russia 185610

Introduction

The Proterozoic rocks of the Shunga district (Karelia, Russia) have attracted interest for over one century because of their high carbon contents and unusual C forms. In addition to their geological fascination, shungites have properties that make them industrially interesting [1].

Shungite (Sh) applications in adsorption of organic matter, bacterial and heavy metal removal, drinking water preparation were widely elaborated in Russia. Hypothesis concerning the role of shungite rocks in natural water systems recovering were also suggested [2].

Nevertheless, up to now the nature of Sh influence on the water chemistry is not quite clear. The most prominent features of shungite / water interaction are the following: pH alteration, extraction of metals and organic, formation of colloidal systems.

Results and Discussion

The most pronounced effects in water treatment were noticed for the so called 'type III' shungite from the Maksovo-Zazhogino deposit (Sh III). This rock is characterized by the inseparability of carbon and mineral parts and the following content (wt.%) : C (20-32), SiO_2 (57.0 -66.2), Al_2O_3 (3.20- 4.45), TiO_2 (0.16 - 0.3), Fe_2O3 +FeO (1.0 - 2.3), MgO (0.4 - 0.8), CaO (0.07- 0.3), K_2O (0.8 - 1.6), Na_2O (0.11- 0.3), MnO (0.01- 0.02), S (0.2 - 0.7). The specific surface area measured by N_2 adsorption BET technique is about 25 m^2 g^{-1} .

Neutral solutions became more acidic after the contact with Sh III. The pH decrease up to 3.8 - 4.4, depending on the particle size and the Sh - water contact conditions was found. Among possible reasons the following might take place: the influence of surface groups, catalytic destruction of organic substances [3], and also electrochemical reactions, in particular [4]

$$4Fe(III) + C + H_2O - CO_2 + 4Fe(II) + 4H$$
$$C\,(O)ads + OH^- \text{---} CO_2 + 2H^+ + 3e^-$$
$$C\,(O)ads + OH^- \text{---} C + H_2O_2 + e^-$$

Extraction of elements from Sh III under different conditions such as exposure time, electrolyte content and concentration was investigated. Among the most intensively extracted substances Ca, Mg, Fe, Mn, Ni, Al, SO_4, Cl, S were found. It was also shown that thermal treatment as well as fine grinding influence greatly on the character of the extraction process. In particular, increase of Na and K and decrease of Al, Fe, Ni, Cr, V extraction were noticed under both kinds of treatment. Our estimations showed that Sh III extraction level is low enough to meet Russian standards for drinking water filter materials.

Formation of colloidal systems is possible as a result of Al, Fe and SO_4 presence in water contacted with Sh III. However, the most unusual colloid is formed due to the Sh rock 'dissolution', so that each micron sized colloidal particle includes carbon and mineral parts.

The close connection between carbon and minerals is the very specific feature of shungite rocks which might reflect shungite origin from carbon - silicone precursor [1]. We assumed that this feature would allow us to use shungite in a treatment of oily wastes. Indeed, we found it possible to clean water from oil up to the very high level - 0.02 - 0.05 mg/l . In this case adsorption capacity was about 60-100 mg/g and the water /sorbent ratio was as high as (1000-1500) : 1, depending on the condition of the process.

Electrochemical treatment of the Sh filters is possible because of Sh rocks high conductivity (1000 S m^{-1}) [5}. The later also allows us to use Electrochemical Impedance Spectroscopy methods [6] to control conditions of the process, such as electrolyte concentration, velocity, and also pressure applied to the shungite filter. We found that one can strongly increase the pH alternation and extraction of Fe(II) as a result of 2-10 V dc. polarization (figure 1).

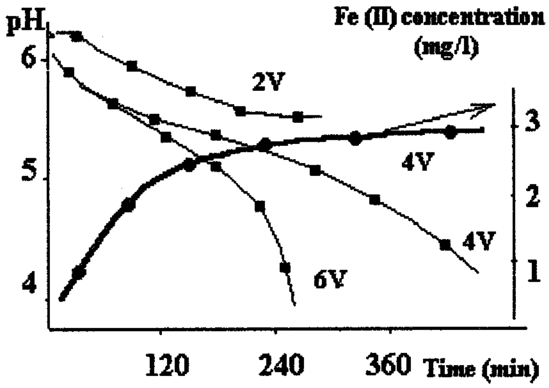

Figure 1. pH and Fe(II) vs. time plots for 2, 4, 6 V shungite filter polarization

Obtained data allowed us to use Sh III as an electrode material in flow-type electrolyzers for drinking water preparation and heavy metals (copper, nickel, cobalt, zinc) removal.

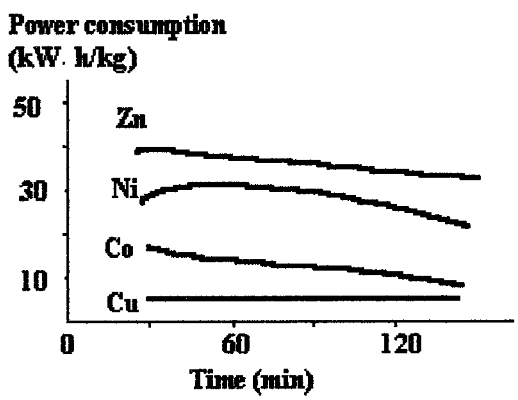

Figure 2. Power consumption vs. time plots for heavy metals electrodeposition process.

In the later case about 90% of metals were removed from sulfate solutions and 100% of nickel was precipitated in a water-ammonia solution. Practically a complete extraction of cobalt and zinc was achieved with a power consumption shown in figure 2.

In addition to the above reduction of Cr (VI) to 10 -100 times less toxic Cr (III) was pointed. The later allows us to elaborate a practical system for Cr (VI) removal. The main advantages of the system are the following : 1) using of low cost adsorbent made of Sh III rock and timber industry waste products combination, 2) elimination of the pH adjustment step, 3) easy utilization of the exhausted adsorbent by thermal oxidation. The ash containing up to 90 wt.% chrome (III) oxide can be used in metallurgy as an abrasive and pigment.

Conclusions

The results allow us to use shungite as a new carbon - mineral adsorbent and also utilize its specific properties: pH alteration, formation of the colloid systems and high electroconductivity in flow-type electrolyzers for heavy metals removal.

Acknowledgments

The study was supported by the Russian Foundation for Intellectual Collaboration (grant "Shungite").

References

1. Kalinin, Yu.K., *Proc. Of the All -Union Society of Mineralogy*, CXIX, N5, 1990, 1-8 (in Russ.)
2. Dyukkiev, E.F, Kalinin, Yu.K., Zaguralskaya, L.M., Zaidenberg, A.Z., in *Geology and Protection of Mineral Wealth of Karelia.* Karelian Research Center, Russ. .Acad. of Sci., Petrozavodsk, 1992, p. 20 (in Russ.).
3. Kalinin, A.I., Theoretical basis for self recovering processes of contaminated water. *Proc. St. Petersburg Center of Ecological Security.*
4. Zaidenberg, A.Z.,. Bormatov, A.A., Beloshapkin, A.A., Dyukkiev, E.F, in *Engineering Problems in Ecology*, (Ext. Abstr. Int. Conf.), Vologda, Russia, 1993, pp. 15-21 (in Russ.).
5. Parfenyeva, L.S., Smirnov, I.A, Zaidenberg, A.Z., Rozhkova, N.N., Stefanovich, G.B., *Russ. Phys. Sol. State*, 1994, 36, pp.234-236
6. Solovov, V.K., Tupolev, A.G., Zaidenberg, A.Z., Zverev, A.A., Kalinin Yu.K., in *MICC-90 Moscow International Composites Conference*, ed. I.N. Fridlyander , V.I. Kostikov. Elsvier Applied Science. London and NY, 1991. pp. 1343-1347.