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PYROLUSITE-RICH TAILINGS FROM NIKOPOL AGAINST ANOXIA?

Anoxia in marine basins is a problem, or is feared to become a problem in several locations. A straightforward remediation would be to blow large volumes of oxygen (or air) into those sub-oxic waters, but that is a tiresome and costly affair. By introducing a solid oxygen donor, it should be possible to attack the anoxia problem for a reasonable period of time in a single and simple operation. An obvious and cost-effective choice would be the use of the mineral pyrolusite (MnO_2). This is one of the commonest manganese ore minerals, and hundreds of millions of tons of manganese tailings containing this mineral are stored in tailings near manganese mines all over the world. A well-known example of such tailings can be found in the manganese mining district near Nikopol/Ukraine. Its use has no harmful effect, as the mineral contains no heavy metals, and even its pore waters are of drinking water quality. The major problem is probably that the reaction of MnO_2 is rather sluggish.

Introduction. Many marine systems, particularly in semi-enclosed and shallow water bodies suffer from anoxia. This is often aggravated by the influx of nutrient-rich waters, leading to phytoplankton blooms. When the plankton dies and sinks to the bottom, their decomposition uses up the available oxygen. Sometimes a remediation is found by blowing air into these anoxic water bodies, like in the Salford Docks area near Manchester, where the waters were heavily polluted by the runoff from sewers. A compressed air injection raised the oxygen level by up to 300 %, leading to a spectacular recovery of the fish stock, both in numbers as in diversity [2]. Although such a remediation is possible, it is costly and energy-intensive, the more so as quite a bit of the air will escape as bubbles, and not take part in the solution of the problem. If one could provide oxygen by using a solid oxygen donor, one can in the course of one simple and cost-effective operation find a remediation for the anoxia. The solid donor can be emplaced at the heart of the problem, and all the released oxygen can play a part in the process. A problem that could occur is the fact that the oxygen release may be sluggish. On the other hand, this makes it possible to spread the effect over a certain length of time, even though the operation itself can be executed rapidly.

Choice of oxygen donor. The material must be cheap, and available in large quantities. A logical choice is the mineral pyrolusite, MnO_2, one of the most common manganese ore minerals. In the form of a commercial manganese concentrate, however, it will not be cheap. All manganese ores occur together with other minerals, so-called gangue minerals. In order to obtain a commercial manganese concentrate, during ore dressing the gangue minerals are separated as completely as possible from the ore minerals. The aim is to produce a commercial concentrate with a minimum Mn-content of 48 %. The success of this treatment, which is expressed by the term recovery, depends on the grain size and the degree of interlocking of the minerals. The gangue minerals are environmentally innocuous minerals like quartz, calcite and clay minerals. Together with the unrecovered manganese minerals these are called tailings which are stored in basins or on tailing dumps. These tailings still contain several % up to 21 % of MnO_2. Manganese ores are notably poor in harmful elements like mercury, arsenic, lead or cadmium.

Nikopol in the Ukraine is a famous manganese mining district. The Nikopol district has been the

world's major manganese producer for a number of years, and is still in operation. It has the largest known manganese resources in the world [1]. The manganese ore is a fine-grained sedimentary ore, which makes that after ore dressing the remaining tailings still contain 21 % of pyrolusite. It is likely that the cost to obtain these tailings will involve no more than its handling and shipping to the point of use. An advantage for the mine is that the area now occupied by the tailings becomes available for other uses.

The total amount of tailings stored in large basins near the Nikopol mines is 170 million tons. This means that they contain 35.7 million tons of pyrolusite. When this amount of MnO_2 is reduced to MnO it releases 6.5 million tons of oxygen. One mole of oxygen (O_2) = 32 gram, and one mole of gas (NTP) takes a volume of 22.7 liter. The amount of oxygen released by the pyrolusite equals 4500 billion liters of oxygen. One m^3 of a solid oxygen donor like pyrolusite contains hundreds of times more oxygen than one m^3 of air.

Transport of the tailings should be easy. The city of Nikopol is situated on the banks of the lower reaches of the river Dniepr, which is navigable for fairly large ships, and reaches the Black Sea near the city of Cherson.

A cure for local anoxia? It is proposed to use these or similar Mn-tailings for the mitigation of anoxia. This is an example of geochemical engineering, which involves the use of geochemical processes and natural materials to solve environmental problems [3]. The first question to be answered is, will their release in deep anoxic waters make a serious contribution to suppress the anoxia? This will depend on the rate of oxygen release by fine-grained pyrolusite under anoxic conditions. The best way to find out is probably to select a test site of a small anoxic polluted lake or a fjord with anoxic bottom waters and spread a cover of pyrolusite tailings over its bottom. Then the changes in oxygen saturation must be monitored. If there is a considerable improvement over a time span of a few months to a few years, the method can be applied for the remediation of anoxia in urgent cases.

Almost certainly marine biologists will raise the question of the environmental damage to marine life that such a geochemical engineering solution might cause. Evidently, potential negative effects on the environment must be closely followed, but from the nature of the pyrolusite itself and its accompanying minerals it seems improbable that this solution will have any negative environmental consequences. Manganese ores are notably poor in heavy metals, and the other minerals are no different than what is found in normal bottom sediments. During an inspection of the mine tailings it was observed that the pore waters inside the Nikopol tailings were of drinking water quality.

Once the questions as to the rate of reaction, and the absence of negative environmental consequences are solved to satisfaction, one can turn the attention to the logistics and the financial consequences of this approach, as well as the selection of the most urgent but small-scale cases of anoxia. It is unlikely that the method can ever be applied to treat large stretches of oceanic anoxic bottom waters. A point of discussion would be the choice between the use of a pyrolusite concentrate (limited volume required, but more expensive) and pyrolusite containing tailings (larger volume, but less expensive).

Conclusions. Oxygen is the most direct answer to anoxia. It is proposed to use a solid oxygen donor in the form of pyrolusite instead of blowing air into the water.

Large volumes of pyrolusite-rich tailings are available near many manganese mines in the world.

No negative environmental consequences are expected by the use of this method.

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ПИРОЛЮЗИТСОДЕРЖАЩИЕ ХВОСТЫ ИЗ НИКОПОЛЯ ПРОТИВ АНОКСИИ?

Аноксия является проблемой морских бассейнов некоторых регионов. Наилучшим средством могло бы быть закачивание больших объемов кислорода (или воздуха) в обедненные кислородом воды, но это довольно хлопотная и дорогостоящая операция. Наиболее простой метод — введение твердого источника кислорода как одиночной операции. Очевидным и эффективным выбором может стать использование пиролюзита (MnO_2) — одного из наиболее распространенных марганцево-рудных минералов. Сотни миллионов тонн содержащих его марганцевых хвостов хранятся в окрестностях марганцевых шахт во всем мире. Хорошо известны примеры таких хвостов в

районе добычи марганца под Никополем (Украина). Их использование не оказывает какого-либо вредного воздействия, поскольку минерал не содержит тяжелых металлов и даже его поровые воды соответствуют по качеству питьевой воде. Основная проблема заключается в том, что реакция MnO_2 проходит очень медленно.

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ПІРОЛЮЗИТВМІСНІ ХВОСТИ З НІКОПОЛЮ ПРОТИ АНОКСІЇ?

Аноксія є проблемою морських басейнів деяких регіонів. Найкращим запобіжним заходом могло б бути закачування великих об'ємів кисню (або повітря) у збіднені киснем води, але це надто складна і дорога операція. Найпростіший метод — введення твердого джерела кисню як окремої операції. Очевидним і ефективним може бути використання піролюзиту (MnO_2) — одного з найпоширеніших марганцево-рудних мінералів. Сотні мільйонів тонн марганцевих хвостів, що містять його, зберігаються в околицях марганцевих шахт у всьому світі. Зокрема, у районі видобування марганцю поблизу Нікополя (Україна). Їх використання не матиме шкідливої дії, оскільки мінерал не містить важких металів і навіть якість його порових вод відповідає якості питної води. Основна проблема полягає у тому, що реакція MnO_2 проходить дуже повільно.