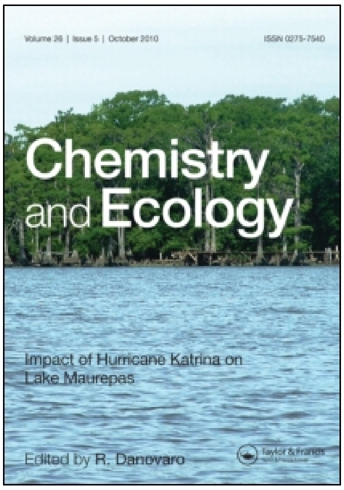

**Chemistry and Ecology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

# Amorphous oxides of manganese as new sorbents of strontium ions

T. A. Marsagishvili[a]; S. A. Kirillov[b]; V. A. Chagelishvili[a]; N.SH. Ananiashvili[a]; D. I. Dzanashvili[a]; T. V. Lesnichaya[b]; V. S. Aleksandrova[b]; M. N. Machavariani[a]
[a] Institute of Inorganic Chemistry and Electrochemistry of Georgian Academy of Sciences, Tbilisi, Georgia [b] Institute for Sorption and Problems of Endoecology, Ukrainian National Academy of Sciences, Kyiv, Ukraine

**To cite this Article** Marsagishvili, T. A. , Kirillov, S. A. , Chagelishvili, V. A. , Ananiashvili, N.SH. , Dzanashvili, D. I. , Lesnichaya, T. V. , Aleksandrova, V. S. and Machavariani, M. N.(2007) 'Amorphous oxides of manganese as new sorbents of strontium ions', Chemistry and Ecology, 23: 1, 87 — 91

**To link to this Article: DOI:** 10.1080/02757540601083906

**URL:** http://dx.doi.org/10.1080/02757540601083906

*Chemistry and Ecology*
Vol. 23, No. 1, February 2007, 87–91

# Amorphous oxides of manganese as new sorbents of strontium ions

T.A. MARSAGISHVILI*†, S.A. KIRILLOV‡, V.A. CHAGELISHVILI†,
N.SH. ANANIASHVILI†, D.I. DZANASHVILI†, T. V. LESNICHAYA‡,
V.S. ALEKSANDROVA‡ and M.N. MACHAVARIANI†

†Institute of Inorganic Chemistry and Electrochemistry of Georgian Academy of Sciences,
11, Mindeli str., Tbilisi, 0186, Georgia
‡Institute for Sorption and Problems of Endoecology, Ukrainian National Academy of Sciences,
13, General Naumov St., 03680 Kyiv, Ukraine

*(Received 31 August 2005; in final form 27 September 2006)*

Samples with the best adsorption properties are selected as a result of investigations conducted on synthesis of manganese-dioxide-based materials and study of their physicochemical properties. Materials were selected on the basis of their low cost and the simplicity of their production technology. In the laboratory the synthesis and analyses of materials was carried out for selected samples. The sorption of a series of elements is studied for a more detailed investigation of materials obtained. The results obtained will promote the synthesis of materials with improved adsorption properties with the aim of their application for purification of water from strontium. It is shown that the most promising way for amendment of manganese oxide is modification of this material using acid-resistant oxides. These oxides are also less expensive than existing sorbents for strontium.

*Keywords*: Strontium; Adsorption; Purification

## 1. Introduction

During the last 150 yr, the global industrial revolution has led to continuous environmental pollution by hazardous wastes and resulted in a deterioration of sources of potable water. Nowadays, the problem of water quality and safety has become even more urgent due to the proliferation of nuclear power plants (NPPs) and the inevitable uncontrolled pollution of minor amounts of radiotracers ($^{235}$U, $^{137}$Cs, and $^{90}$Sr in the first place), to say nothing about numerous NPP accidents, from insignificant ones to Three Mile Island and Chernobyl. High-level radioactive waste accumulating as a by-product of nuclear technologies has to be disposed of in an economical and safe manner, and the after-effects of their possible leakages have to be effectively eliminated.

---

*Corresponding author. Email: tmars@geo.net.ge

*Chemistry and Ecology*
ISSN 0275-7540 print/ISSN 1029-0370 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540601083906

Water purification can be performed using processes employing numerous physical and chemical methods like precipitation and co-precipitation, distillation, filtering, osmosis and electro-osmosis, dialysis and electro-dialysis, sorption and electro-sorption, etc. One of the most powerful, and therefore the most promising, technologies of water management during the 21st century is the technology based on ion-exchange resins, especially, ion sieves or, in a broader sense, selective inorganic ionites. Ion-exchange sorption is equally (and successfully) applicable, on small and large scales, to concentrated and infinitely diluted solutions.

Ion-exchange resins are polymeric acids (alkalies) whose protons (hydroxyls) can be substituted by cations (anions). These adsorbents do not 'select' incoming particles, binding all of them irrespective of their chemical nature. Moreover, ion-exchange resins are not selective for any specific cations or anions: according to the mass action law, they just absorb those particles whose content in the solution is greater.

Ion sieves are natural and synthetic crystalline materials like aluminosilicates (zeolites), clay minerals, mesomorphous silicates, and transition metal oxides, both anhydrous and of varying degrees of hydration. Unique properties of these materials arise due to the presence of one- or two-dimensional cavities (channels or layers) in the structure accessible to guest ions, so that such crystals are often referred to as porous crystals [1–4]. Numerous natural (chabazite and clinoptilolyte) and synthetic materials of this kind (sodium nonatitanate, silicotitanates, and substituted pharmacosiderites) have been probed for the treatment of wastes containing $^{235}$U, $^{137}$Cs, and especially $^{90}$Sr.

Selective adsorption of ions on natural and synthetic inorganic materials is not limited to ion-exchange mechanisms. Quite often, the key role is played by other (chemical) properties characteristic of each particular adsorbent, e.g to the ability of molecular groups on its surface to complex formation or redox reactions with adsorbed ions, etc. In other words, extraordinary features of selective inorganic adsorbents cannot be considered in simple physical (geometrical) terms; they imply manifold physical and chemical phenomena.

The aforementioned problem is especially vital for decontamination of water polluted with strontium. The best-known $Sr^{2+}$-ion exchangers with distribution constants $K_d^{Sr} \cong 4 \times 10^4$ and selectivity factors for the sorption of $Sr^{2+}$ ions in the presence of $Ca^{2+}$ ions $K_{Sr/Ca} \cong 50$ are usually based on harmful antimony oxide and therefore cannot be employed for processing potable water. Other kinds of $Sr^{2+}$-ion exchangers may demonstrate even better characteristics, but their effectiveness decreases significantly, depending on pH and the presence of complexing agents in solutions. The search for new materials capable of effectively removing strontium from potable and waste water is one of the great challenges of contemporary materials design.

According to the literature, several natural and synthetic manganese dioxides [5–7] demonstrate selectivity and a reasonable exchange capacity towards $Sr^{2+}$. Regarding manganese-oxide-based composites, one may consider titanium as one of the most prospective modifiers, bearing in mind its ion-exchange properties towards isotopes of uranium. In addition, titanium itself exhibits reasonable ion-exchange properties towards $Sr^{2+}$. Good ion-exchange characteristics of individual $TiO_2$ and $MnO_2$ mean that mixed oxides, viz., $x\mathrm{MnO_2} \cdot y\mathrm{TiO_2}$, may serve as adsorbents for two major radioactive pollutants, $^{235}$U and $^{90}$Sr.

Such multi-component materials may be of great value in practice, from purification of drinkable water in the case of minor contamination to decontamination of circulating water in the case of nuclear power-plant accidents, as well as aqueous wastes resulting from chemical extraction processes for the production of nuclear weapons and fuels. Water-management applications remain especially vital for Ukraine and southern Belarus: the reader is reminded that the sources of potable water in these regions, especially in rural districts, are contaminated by $^{90}$Sr, and portable water-purification systems may significantly improve the quality of life of tens of thousands of people.

Advanced manganese-dioxide-based materials have good prospects for future use, as their raw materials are easily available. Deposits of manganese ores are found all over the world (Austria, Bulgaria, Italy, Portugal, Romania, USA, etc.) and especially in Georgia (Chiaturi) and Ukraine (Dnipropetrovsk region).

## 2. Results and discussion

### 2.1 *New sorbents for radionuclides*

Novel materials based on manganese dioxide and oxides of manganese and titanium have been synthesized [8, 9] and tested by us.

Physical and chemical studies (scanning electron microscopy, X-ray studies, and thermal analysis) demonstrate the amorphous nature of the samples obtained. Beginning at $t = 450\,°\mathrm{C}$, X-ray data for Mn–Ti samples demonstrate the appearance of peaks attributable to rutile and anatase, depending on temperature. Data for a typical binary sample, obtained from X-ray analysis and use of a card index from the American Society for Testing Materials (ASTM 21-1276), are listed in table 1. That is, the process of crystallization of mixed oxides of manganese and titanium begins with segregation of crystalline titanium oxides.

Furthermore, as in the case of a single component, the surface area of composites obtained has been measured, since with this parameter one may determine the application area for the materials. Recall that single titanium oxides have fairly high surface areas (up to $S_{\mathrm{sp}} = 675\,\mathrm{m}^2\,\mathrm{g}^{-1}$), and surface areas of manganese oxides have an area of about 24–50 $\mathrm{m}^2\,\mathrm{g}^{-1}$. Mechanical mixing of these oxides should result in additive surface areas, whereas the formation of an amorphous ‘compound’ should lead to non-additivity. The values of the surface area reach a maximum for samples with a Ti:Mn ratio of 50 : 50 and have an $S_{\mathrm{sp}}$ varying between 190 and 530 $\mathrm{m}^2\,\mathrm{g}^{-1}$. It is significant that the value of the surface area is influenced by both the synthetic procedure and the washing method. Samples washed by acidified water have surface areas almost twice as large as those washed by distilled water.

Large values for specific areas determine the high sorption affinity of materials, so that for most prospective samples, distribution coefficients towards strontium have been found.

The specific surface areas ($S_{\mathrm{sp}}$) and sorption characteristics for strontium extraction (capacity $A_{\mathrm{Sr}}\,\mathrm{mg\,g}^{-1}$ and distribution coefficient $K_{\mathrm{dSr}}\,\mathrm{ml\,g}^{-1}$) were studied for these samples.

Table 1. Data for a roentgenophase analysis of a binary sample of $TiO_2 : MnO_2 (1 : 1)$.

| Sample $TiO_2 : MnO_2 = 1 : 1$ | | ASTM 21-1276 $TiO_2$ | |
|---|---|---|---|
| $d\alpha/n$ | $I/I_0$ | $d\alpha/n$ | $I/I_0$ |
| 4,92 | 30 | – | – |
| 4,23 | 37 | – | – |
| 3,2 | 100 | 3,25 | 100 |
| 2,46 | 50 | 2,48 | 50 |
| 2,16 | 30 | 2,18 | 25 |
| 2,03 | 12 | 2,05 | 10 |
| 1,85 | 17 | | |
| 1,67 | 65 | 1,68 | 60 |
| 1,62 | 20 | 1,47 | 2 |

Table 2. Properties of amorphous oxides of manganese and titanium.

| $N$ | Sample | $S_{sp}$ ($m^2\,g^{-1}$) | pH | $C_{Sr\,eq}$ | $A_{Sr}$ ($mg\,g^{-1}$) | $K_{dSr}$ ($ml\,g^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | $MnO_2$ | 195 | 6.64 | 1 | 13.1 | 13 100 |
| 2 | $MnO_2$ | 273 | 6.38 | 4.4 | 12.76 | 2900 |
| 3 | $MnO_2$ | 3 | 8.36 | 0.2 | 13.18 | 65 900 |
| 4 | $MnO_2$ | 6 | 7.58 | 0.5 | 13.15 | 26 300 |
| 5 | $TiMn/O_2$ | 78 | 7.99 | 0.4 | 13.16 | 32 900 |
| 6 | $TiMn/O_2$ | 184 | 7.73 | 0.5 | 13.15 | 26 300 |
| 7 | $TiMn/O_2$ | 164 | 10.76 | 0.2 | 13.18 | 65 900 |
| 8 | $TiMn/O_2$ | 281 | 7.84 | 1.2 | 13.08 | 10 908 |

The conditions for strontium sorption were as follows. The concentration of initial solutions on $Sr^{2+}C_{in} = 132\,mg\,l^{-1}$, 0.1 N $NaNO_3$ served as background; a sample (mass of sample, $m = 0.2\,g$) of oxides was flooded with the investigated solution ($V = 20\,ml$). The contact time for periodic shaking was 3 d; oxides were then filtrated, the equilibrium pH was measured, and the concentration of strontium ions, $C_{Sr\,eq}$, was measured on an atomic-adsorption spectrophotometer.

Calculations of specific capacity were carried out using the formula:

$$A = \frac{C_{in} - C_{eq}}{m} V,$$

and $K_{dSr}$, the distribution coefficient, using the formula:

$$K_{dSr} = \frac{C_{in} - C_{eq}}{C_{eq}} \frac{V}{m}.$$

Table 2 displays that the values of the specific surface are higher than average values for titanium-manganese oxides, suggesting high sorption capacity for these two types of oxides.

From the results of sorption studies, crystalline samples of binary manganese and titanium oxides do not absorb strontium from model solutions. For this kind of material, the distribution coefficients, $K_d$, vary from 5 to 20 $ml\,g^{-1}$. For binary amorphous systems, the $K_d$ values vary widely, depending on numerous factors, including synthetic conditions. These sorbents can be utilised by means of calcination at 400 °C.

## 3. Conclusion

On the basis of amorphous manganese dioxide, new materials have been developed that can sorb ions of strontium. Sorbents on the basis of manganese and titanium dioxides have also been obtained. From an investigation of the properties of materials obtained, it can be concluded that amorphous oxides of manganese and mixed oxides of manganese–titanium synthesized by specific technologies constitute rather effective sorbents for strontium ions.

## Acknowledgements

We are deeply thankful to STCU for financing the work (Project GR-85(j)). We also acknowledge Clean Black Sea Working Group (EC SSA project INCO-CT-2004-003510) and especially Dr Antonio Pusceddu for a useful discussion.

## References

[1] S.L. Suib. *Chem. Rev.*, **93**, 803 (1993).
[2] D.M. Antonelli, A. Nakahira, J.Y. Ying. *Inorg. Chem.*, **35**, 3126 (1996).
[3] S.L. Brock, N. Duan, Z.R. Tian, O. Giraldo, H. Zhou, S.L. Suib. *Chem. Mater.*, **10**, 2619 (1998).
[4] Q. Feng, H. Kanoh, K. Ooi. *J. Mater. Chem.*, **9**, 319 (1999).
[5] S.M. Hasani, Najamuddin, M. Ikram. *Sep. Sci. Technol.*, **32**, 1945 (1997).
[6] G.V. Leont'eva, V.V. Vol'khin. *Zh. Prikl. Khim.*, **44**, 2615 (1971).
[7] V.V. Vol'khin, G.V. Leont'eva. *USSR Patent* #265866 (1973).
[8] Application for the grant of the Patent of Georgia, 8817/02, 30 May 2005.
[9] Application for the grant of the Patent of Georgia, 8818/02, 30 May 2005.