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"Heat, Gas and Water Technology"

FERROMAGNETIC SORBENTS AND THEIR POTENTIAL FOR COLLECTING POLLUTION WITH SPILLED OIL PRODUCTS

Summary of the Doctoral Thesis

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DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OFDOCTOR OF ENGINEERING SCIENCES

To be granted the scientific degree of Doctor of Engineering Sciences, the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on 8.04.2018, 12.00 AM. at the Faculty of Civil Engineering of Riga Technical University, 6B Ķīpsalas Street, Room 250.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Name Surname ……………………………. (signature)
Date: ………………………

The Doctoral Thesis has been written in Latvian. It consists of Introduction; 3 chapters; Conclusion; 70 figures, 16 tables, 1 appendices, the total number of pages is 98. The Bibliography contains 166 titles.

ANNOTATION

Juris Treijs has worked on his Thesis "Ferromagnetic Sorbents and their Potential for Collecting Pollution with Spilled Oil Products" at Riga Technical University and in collaboration with Rezekne Academy of Technologies.

The problem of water decontamination from oil pollution is becoming increasingly topical nowadays because of the growing scale of accidents associated with oil spills from large-tonnage vessels and offshore drilling. Fuel leak from oil depots, petrochemical plants, and fixed tanks of large road transport companies inevitably causes pollution getting into the ground and underground waters, as well as into river basins.

Different types of sorbents are used for elimination of the pollution. Therefore, the issue of development of new sorbents is always topical.

The Thesis is dedicated to the development of new sorbents having ferromagnetic characteristics and to researching what can be used for the collection of spilled oil pollution. Ferromagnetic properties of sorbents allow selective collection of pollution by means of modern technological solutions. The Thesis focuses on the use of recycled resources and of industrial waste, which can be applied for creation of porous, including adsorbent materials. In the course of the study, powdered, floating and ferromagnetic characteristics-bearing sorbents, their extraction at the laboratory level from residues of industrial processes were designed and explored. Positive results have been presented by *Comsor 125* as one of the newly acquired sorbents, being capable to absorb up to 1.5 kg oil pollution per 1 kg sorbent. The sorbent model and methodology for its development was created in the course of the work. It has a floating element in its centre, connected with ferromagnetic particles. Use of ferromagnetic particles represents a prospective direction in the water purification sector from the light types of oil pollution. It will make possible collecting of pollution together with ferromagnetic powder from the water surface by means of mechanical and electromagnetic equipment.

In the course of the work, technologies and appliance were developed for spraying of powdered sorbents above the water surface contaminated with oil products. A stand was created to reduce the human factor during performance of the experiments, which used three permanent voltage magnets and electromagnetic equipment for collection of the oil product contamination from the water surface and below the water level in small depths. The Thesis focuses on recovery and reuse of the sorbents.

New products were developed on the basis of extractable sludge to be used as fuel, fuel elements for thermal cutting of concrete and retrieving metal from solutions that can potentially add to the list of products manufactured in Latvia for internal consumption, as well as for export. The results presented in the Thesis are protected by two LV patents.

The findings presented in the Thesis have been published in 6 scientific articles and 8 scientific reports at international conferences.

INTRODUCTION

Nowadays increasingly growing problem is represented by water decontamination from pollution with oil and oil products (OPs) due to accidents involving oil spills from large-tonnage tankers and from offshore drilling, which are taking place more often. Spills of fuel and other OPs in oil depots, petrochemical plants, from fixed tanks of large road transport undertakings, passing vessels and ships present at the quayside in navigable river basins and port aquatoria, and oil pipeline accidents inevitably cause pollution getting into the ground, underground waters, as well as river basins. Therefore, problem of elimination of the OP pollution from the water surface is of global nature.

Topicality of the theme

Spills of oil products (OPs) into the water represent a very serious environmental disaster, the consequences of which can be devastating for every living being. Small living organisms, flora, birds, fish and many marine mammals are suffering from spills of OPs [1].

Oil is a product of extended breakdown and, when released, very quickly covers the water surface with a dense oil film layer, which hinders access to air and light. It begrims around bird feathers and results in birds losing their ability to maintain heat, to swim and to fly. In order to avoid the above, OPs spilled in the water have to be removed quickly [2].

There are various methods for water decontamination from pollution with oil products: mechanical, physical-chemical and biochemical methods. Each group has its own advantages and disadvantages, concentration and the total pollution amount areas where those are especially effective. In any particular case, complex and multi-layered decontamination technologies must be used, where any method prevails [3].

The aim of the Thesis is to develop a sorbent with ferromagnetic properties, examine its properties and possibilities to use in the collection of pollution with spilled oil products, as well as its further use and utilization options.

Tasks of the Thesis

- Literature analysis regarding the existing sorbents, collection techniques of the oil products, as well as further processing of the collected oil products.
- Development of a sorbent with ferromagnetic properties and examination of its properties.
- Development of a method for water decontamination by means of ferromagnetic sorbent.
- Development of a new sorbent functioning model and performance of its analysis.
- Development of the sorbent recovery and recycling method.
- Development of an experimental pilot equipment, which ensures the collection of oil products through magnetic fields.
- Development of recommendations for recovery and reuse of the sorbent.

Theses proposed for defence

1. New materials (ferromagnetic sorbents).
2. Combined sorbent model with ferromagnetic properties.
3. New technological solutions (equipment and technologies for spraying and collection of the sorbent).
4. New proposals for use of the collected materials (regeneration, fuel, antiseptics).
5. New product development (NPD) – use of the sludge as fuel in thermic concrete cutting, sorbents for copper extraction from solutions).

Scientific novelty of the Thesis

- New methodology developed for creation of new types of sorbents with ferromagnetic properties for sorbtion of oil products.
- A process model proposed for sorption of oil product films from the water surface by means of ferromagnetic particles.
- Analysis provided regarding the impact of the composition and properties of ferromagnetic sorbents on the sorbtion process.
- New methods offered for the production of composite sorbents with ferromagnetic properties.
- New methods proposed for sorbent spraying and sludge removal from water by means of magnetic and electromagnetic devices.
- Data obtained for thermogravimetrical and differential thermal analysis of iron powder-base sorbent and the collected sludge in the temperature range up to 1000 degrees.
- Proposal for use of the collected OPS (oil product sludge) as high temperature fuel product.

Practical novelty of the research

- Some new composite sorbents (*Comsor 125*, *Comsor M,* etc.) developed with magnetic properties.
- New types of ferromagnetic sorbents developed on the basis of use of technological residues and natural raw materials.
- Stands developed, designed and tested for spraying sorbents on the water surface contaminated with oil products for study of the processes.
- Stands developed, designed and tested for collection of the sludge by means of magnetic and electromagnetic equipment.
- New sorbent recovery and reuse technology proposed.
- New ways for the use of sludge proposed, sorbents obtained with oil products (for concrete cutting with gas flame, production of fuel emulsions and copper extraction from solutions).

The novelty of research is approved by two Latvian patents (see Annex 1.2).

Approbation of Thesis

Pursuant to the results of research carried out in the present Thesis, 16 scientific papers have been published in Latvian, Russian and English, including 6 scientific articles and 8 scientific report theses for international conferences, and 2 patents have been obtained. They have examined the oil product sorption processes, creation of powdered ferromagnetic sorbent and characteristics thereof.

International publications in reviewed editions

1. Treijs, J., Teirumnieks, E., Mironovs, V. Environmental pollution with oil products and review of possibilities for collection thereof. Vide. Tehnoloģija. Resursi: VIII starptautiskās zinātniski praktiskās konferences materiāli: Rezekne, Latviea, 2011, 301.–309.
2. Lapkovskis, V., Mironovs, V., Treijs, J., Teirumnieks, E. Collection of spilled oil products by means of ferromagnetic powder materials. Riga Technical University 53rd International Scientific Conference: Dedicated to the 150th Anniversary of Riga Polytechnical Institute / RTU Alumni: Digest: Riga, Latviia, 2012, 391.
3. Mironov, V., Zemchenkov, V., Lapkovskiy, V., Treis, Y., Savich, V. Investigation of powder ferromagnetic sorbents properties for petroleum collection from water surface

(Исследования свойств порошковых ферромагнитных сорбентов для сбора нефтепродуктов с водной поверхности) Ekologicheskij vestnik, 2013, 1(23), 32–40.
4. Treijs, J., Teirumnieks, E., Mironovs, V., Lapkovskis, V., Šiškins, A. Investigations of properties of powdered ferromagnetic sorbents. In Proceedings of the 9th International Scientific and Practical Conference "Environment. Technology. Resources": Rēzekne, Latvija, 2013, 1, 95–100.
5. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Teirumnieks, E. Ferromagnetic composite for oil spill collection, its properties and morphology. International Conference "Innovative Materials, Structures and Technologies": Riga, Latviia, 2013, 46 p.
6. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Korjakins, A. Ferromagnetic sorbents for collection and utilization of oil products. Key Eng. Mater., 2014, 604, pp.122–125.

Scientific publications (indexed in SCOPUS data base)
1. Treijs, J, Teirumnieks, E., Mironovs, V, Lapkovskis, V., Shishkin, A., "Investigations of properties of powdered ferromagnetic sorbents," in Vide. Tehnologija. Resursi - Environment, Technology, Resources, 2013, Vol. 1, pp. 95–102.
2. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Korjakins, A. "Ferromagnetic Sorbents for Collection and Utilization of Oil Products," Key Eng. Mater., Vol. 604, pp. 122–125, 2014. doi:10.4028/www.scientific.net/KEM.604.122).

Journals
1. Mironov, V., Zemchenkov, V., Lapkovskiy, V., Treis, Y., Savich, V. Investigation of powder ferromagnetic sorbents properties for petroleum collection from water surface (Исследования свойств порошковых ферромагнитных сорбентов для сбора нефтепродуктов с водной поверхности). Экологический вестник. Nr. 1 (23). Minsk, Belorussia, 2013, 32–40.

Participation at conferences and congresses
1. Mironovs, V., Lapkovskis, V., Treijs, J. Ferromagnetic sorbents for collection and utilization of oil products. International Scientific Conference "Materials Engineering", Kaunas, Lithuania, 2011.
2. Šiškins, A., Treijs, J., Mironovs, V., Lapkovskis, V. Investigation of Ferromagnetic Metal – Ceramic Adsorbent Materials. 8th International Conference "MET – 2013". Riga, Latvia, 19 June 2013.
3. Lapkovskis, V., Mironovs, V., Treijs, J. Criteria methods in evaluation of peat materials properties. 8th International Conference "MET – 2013": Riga, Latvia, 19 June 2013.
4. Treijs, J., Mironovs, V. Investigations of Properties of Powdered Ferromagnetic Sorbents. 9th International Scientific and Practical Conference "Environment. Technology. Resources", Rezekne, Latvia, 22 June 2013.
5. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Korjakins, A.. Ferromagnetic Sorbents for Collection and Utilization of Spilled Oil Products. International Scientific Conference "Baltmattrib 2013". Riga, Latvia, 14 November 2013.
6. Treijs, J., Teirumnieks, E., Lapkovskis, V., Mironovs, V. Sorbents for Collection of Oil Products. 4th Symposium "Verbundwerkstoffe und Werkstoffverbunde". Dresden, Germany, 18 November 2013.
7. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Teirumnieks, E., "Ferromagnetic composite sorbents for oil spill collection, its properties and morphology. International Conference "Innovative Materials, Structures and Technologies". Riga, Latvia, 2013.

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9. Shishkin, A., Mironovs, V., Lapkovskis, V., Treijs, J., Teirumnieks, E. Ferromagnetic composite sorbents for oil spill collection, its properties and morphology. International Conference "Innovative Materials, Structures and Technologies", Riga, Latvia, 2013.
10. Treijs, J., Mironovs, V. Increase of efficiency of application of ferromagnetic sorbents at collection of oil products spilled in water. 6th International Symposium: Porous permeable materials: technologies and products. Minsk, Rakov, Belorussia, 19 October 2017.

National patents:

1. Šiškins, A., Mironovs, V., Treijs, J., Baroniņš, J. Sorbents ar feromagnētiskām īpašībām. Pat. LV 14822 B (20.06.2014.).
2. Šiškins, A., Mironovs, V., Treijs, J., Feromagnētiskais sorbents. Pat. LV 14820 B (20. 06. 2014.).

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1. COLLECTION OF OIL PRODUCTS (ANALYTICAL PART)

1.1. Oil Pollution Problems

Oil is a mixture of hydrocarbons having different molecular weights and diverse boiling temperature and density of 0.82–0.92 g/cm^3 [21]. With distillation method it is divided into separate oil products (OPs): petrol containing some lightest hydrocarbons, naphta containing hydrocarbons with high numbers of carbon atoms, kerosene, and gas oil.

After these products are distilled, a black, viscous liquid – heavy fuel oil – is left over from oil. Lubricant oils are obtained from heavy fuel oil by means of distillation, for lubrication of different mechanisms. Distillation is carried out at a reduced pressure, in order to reduce hydrocarbon boiling temperature and to avoid decomposition when heated. Non-volatile dark mass – goudron to be used for street asphalting – is left over after the oil distillation. The most important products to be derived from oil are shown in Table 1.1 [22].

Solid hydrocarbons are extracted from certain varieties of oil – so-called paraffin (used, for example, in candle-making) and vaseline, which is a mixture of liquid and solid hydrocarbons [23]. Apart from processing in lubricating oils, the heavy fuel oil is used as fuel in plant boiler spaces, where it is administered with the help of nozzles.

Table 1.1

Main Types of Oil Products

<table>
<tr><th colspan="3">Types of oil products</th><th>Boiling temperature, °C</th></tr>
<tr><td colspan="3">Petrol</td><td>40–200</td></tr>
<tr><td colspan="3">Naphta</td><td>25–50</td></tr>
<tr><td colspan="3">Kerosene</td><td>120–240</td></tr>
<tr><td colspan="3">Gas oil</td><td>150–310</td></tr>
<tr><td rowspan="4">Heavy fuel oil</td><td>Lubricatin g oils</td><td>Spindle oil, motor oil, cilinder et al. oils</td><td>300–350
350–400</td></tr>
<tr><td colspan="2">Vaseline</td><td>230–255</td></tr>
<tr><td colspan="2">Paraffin</td><td>250–270</td></tr>
<tr><td colspan="2">Goudron</td><td>380–420</td></tr>
</table>

Heavy fuel oil shall mean a mixture of organic compounds containing hydrocarbons (having molecular weight of 400 to 1000), oil resin (having molecular weight of 500 to 3000 and more), asphaltene, karben and metals (V, Ni, Fe, Mg, Na, Ca). Physical and chemical properties of the heavy fuel oil are dependent on the original oil composition and distillation of the distillate fractions and their typical data are as follows: viscosity 8–80 mm^2/c (at 100 °C), density 0.89–1 g/cm^3 (at 20 °C), solidification point 10–40 °C, sulphur content 0.5–3.5 %, ashes up to 0.3 %, low calorific value 39.4–40.7 MJ/mol.

Operations of industrial companies, oil depots, rail and road transport, as well as maritime and river vessels result in significant quantities of OP waste in the form of fuel waste, bottom sediments, exhaust oils. These products are posing high danger to the environment [25], in particular in the case where these products are present in large amounts.

1.2. Methods for Collection of the Oil Products

Decontamination of nature from oil can be divided into three modes [32], [33]:

1) water decontamination from OPs;
2) decontamination of coastal zone;
3) decontamination of polluted soil.

While according to elimination methods of the oil product spills they can be divided according to the collection/liquidation principle:

1) mechanical type;
2) chemical type.

Liquidation of the consequences for oil product spills by mechanical means – booms

In liquidation of the consequences of oil spills priority is given to mechanical collection of oil products, first, via their localization. The most common type for localization of spilled oil is enclosing further spread of the pollution with booms and then collection thereof by means of mechanical appliances.

Containment booms (booms) are consisting of floating barriers provided for localization of distribution of OPs discharged in water and transportation thereof at a small distance [34].

General boom structure is shown in Figs. 1.1. and 1.2.

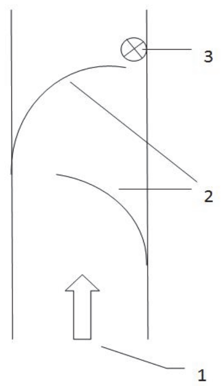


Fig.1.1. Cross-sectional draft of the booms:
1 – plastic material, which performs the OP holding function;
2 – floating material, which performs retaining on the water surface;
3 – sinking material, which performs the plastic material (1) tensioning function by not allowing its spinning. Blue line shows the water level.

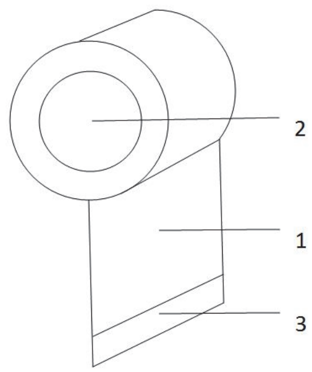


Fig. 1.2. Principal scheme for operation of the containment type booms:
1 – river stream direction;
2 – adsorbent booms;
3 – mechanical oil collection.

Mechanical OP removal from the water surface

After localization of the oil products their collection may be commenced. Most commonly it is carried out by means of mechanical devices – skimmers. There are several types of receivers: floating, screws, rope, tape, etc. [33], [38].

All the floating receivers are essentially pumps, inlet of which is located under the water level and, when operation starts, they commence drawing in the oil film formed on the water surface.

Screw receivers are operating in the same way as all the receivers described below, they have one peculiarity reflected in their name – the receiver component, which receives the oil product and delivers it to the storage bin.

OP collection from the water surface by means of chemical substances

In exceptional cases, in order to prevent pollution of particularly sensitive maritime coastal areas with OP, spilled oil can be treated with dispersants, unless authorisation has been issued for use of disperants and oil spill has not been emulsified yet [39]. Dispersants are represented by various types of chemical detergents, which are sprayed over oil spots from aircrafts or boats. The chemicals are splitting oils in very tiny drops, which are vertically distributed in the water. Use of dispersants speeds up the physical and chemical degradation processes, which would have taken place naturally. Dispersants can be sprayed directly over oil spots by means of special floating stations or aircrafts. Impact of dispersants on the oil products in water and operating principle at the molecular level is generally shown in Fig 1.3 [40].

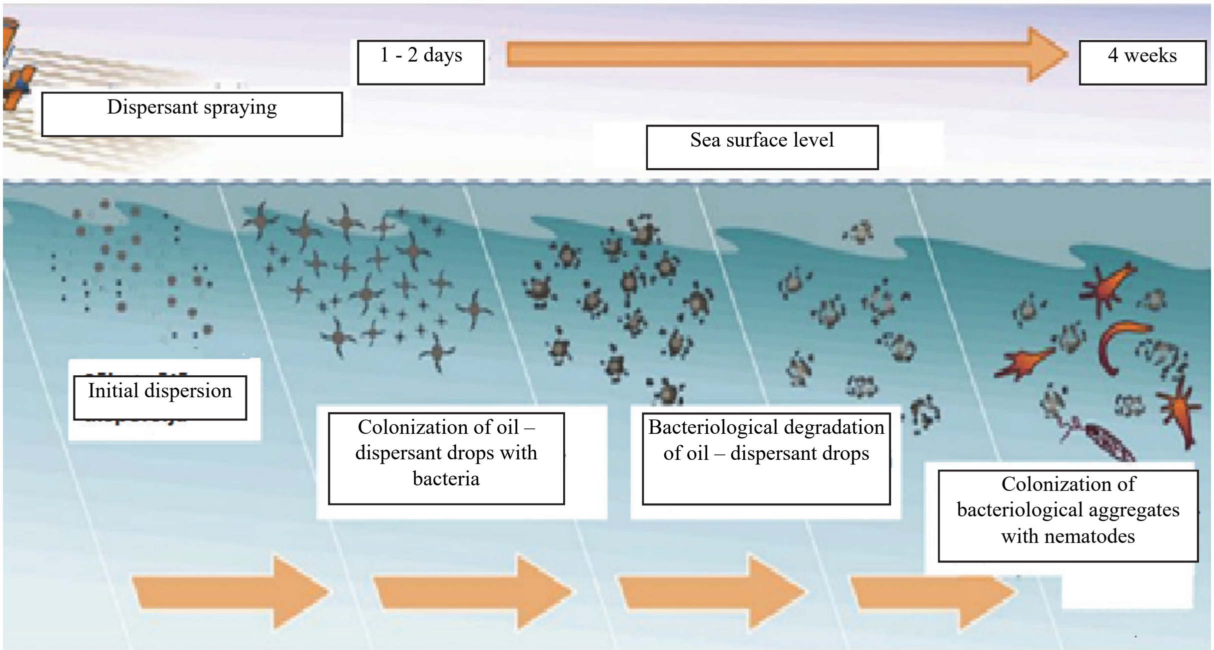


Fig. 1.2. Stages of exposure of spilled oil products to dispersant.

Decontamination of polluted coastal area

Three basic methods are practically applied for restoration or protection of a polluted coastal area [40].

1) If the circumstances warrant it, containment can be installed between the oil slick and the shoreline, thus preventing oil pollution even to reach the shore.
2) If it is not possible to set up a containment, then oil slick is sprayed with chemicals in order to avoid splitting of hydrocarbons on the beach. Such treatment prevents the disintegrated oil to adhere to the sand and to the stones situated on the shore, facilitates its collection process, or also promotes natural degradation.
3) If the beach is contaminated, there are two options: treatment of the coastline with the already mentioned chemicals or mechanical collection of oil.

One of the collection facilities is of a trailer type, which is dragged by any construction machines, for example, tractor. This appliance decontaminates sand or grass with springs cut across points, penetrating into the sand and bringing oil lumps into the mouldboard further diverted into hydraulic tank on the machine rear.

Decontamination of polluted soil

Removal of pollution from contaminated soil is carried out by physical and chemical means. These processes are trying to separate harmful substances from soil, sand or abrasive material. Separation may be done using different methods [42].

Separation by means of gravity. This process may be based on different densities between the solution stages. The size of device and effectiveness of decontamination by means of gravity is dependent on speed adjustment of the spread of oil or its products, size of the substance particles, density difference, viscosity and concentration of the particles. Separation with gravity is applied also in order to dispose of immiscible oil layers and to classify particles with different dimensions. Typically coagulation and flotation is used beforehand in order to increase the size of the particles, which facilitates the separation process.

Physical separation by means of sieve. Separation process uses sieves of different sizes and screens in order to effectively concentrate oil and its products in smaller quantities. Physical separation is based on the fact that organic and inorganic substances are mutually connecting both chemically and physically, particularly it is expressed in clay and sludge. Clay and sludge particles are physically attached to coarse sand or soil, which perfectly concentrates OP in a little volume unit, hence it is easier to process. The biggestt advantage of physical separation is that a high level of purification can be achieved with a relatively small number of devices. However, there is a range of factors present, which may limit effectiveness and practicality of both these processes. One of these is high clay and moisture content of the soil, which increases the decontamination costs. In separation by means of gravity the processes are based on different specific weights of solids and solution.

Soil washing. In the course of soil washing process the water is saturated with the washing agent, surface active substances, pH regulatory substances or colloid agents, which assist in separation of organic substances. During the soil washing process the poisons are separated in two ways – by releasing or by creating other substances, as well as by collecting the same in small quantities in high concentrations [43].

The concept of decontamination of the polluted soil with particulate matter reduction is based on the fact that the OP has a tendency towards physical or chemical binding with clay, sludge or organic soil particles. While the clay and sludge is bound to the sand with natural methods such as compression and adhesion. Washing process separates not only clay and sand from the soil, but also reduces the oil product particles in soil to make it easier to work with the same afterwards. This method also contains a number of factors, which may limit effectiveness and applicability of the process. When washing the soil contaminated with OP, many and different unnecessary solutions (e.g. organic substances + metals) may emerge, which requires additional processing, and therewith the costs are increased and the purification process gets complicated. High humus content of the soil can increase major costs, because it is difficult to separate humic substances in loamy soils. Saturated water also requires additional processing and demobilisation.

1.3. Sorbents

Different sorbents are widely used for collection of OPs spilled in water, hence natural and artificial [51], [52] sorbents are used as materials with a developed surface. They are charged with a number of requirements: maximum available sorption volume, flowability, buoyancy, small weighing down, safety to the environment, resistance to wear (in the event when used in releasable filters), recovery option, etc. (Table 1.2).

Use of asbestos paper and cardboard for water decontamination from OPs [53] is known. In this case, the sorbent recovery is carried out through heating. Polymer sorbents are widespread, which can be recovered by solvents [54] or by extraction [55].

Table 1.2

Main Characteristics of Bulk Sorbents

Properties	*Units of measurement*	*Range*
Sorbtion volume	g/g	1.5–50
Bank density	g/cm^3	2.00–3.80
Fluidity	s	10–20
Moisture	%	Up to 10
Buyoancy	Twenty-four hours	From 2 to 10

Hydrofobised basalt fibre base sorbents are recovered also by squeezing out or by incinerating OP residues [56]. Shavings and sawdust placed in permeable fabric casing [57], to be used as sorbent, may be disposed of by incineration, at the same time producing energy. Granular activated carbon, one of the most wide-ranging sorbents, is also used in water decontamination from OPs [51], [52], [58], [59]. Whereas activated charcoal is expensive as sorbent, which results in its typical use only for additional processing of drinking water.

All the previously mentioned sorbents have another common disadvantage: difficulty in sludge removal from water surface after implementation of the sorption process. It is mainly carried out mechanically – with scraper blades, and rollers. Sometimes sludge pumps [60] are used, working in the increased area of concentration of OPs confined with the boom containment.

Many existing methods for the collection of spilled OP residues facilitate the use of various emulsifiers, including those on the surfactant basis. These methods are related to environmental chemical pollution, their characteristic trait is difficulties in full utilization of materials and increased expenses.

1.4. Overview of Ferromagnetic Sorbents

Allocation of magnetic properties to the sorbents can provide considerable efficiency increase thereof, because it opens up a possibility to introduce sorbents in the environment to be decontaminated in the form of dispersity phase at the controllable surface and to extract from the environment by means of magnets and electromagnets [69]–[70]. Papers [71]–[72] consider a possibility to use disperse ferromagnetic sorbents (FMS) for the collection of oil and other oil products at the bottom of watercourses. Several publications have provided new proposals regarding sorbents having magnetic properties and described possibilities of their use in the collection of light fractions of OP products spilled in water. Such operations are carried out in a number of countries. For example, one of the methods is proposed in Odessa (Ukraine) [73].

The Thesis describes “naftaclean” – a product, which is used for the collection of spilled oil. A variety of organic fibre, for example, lignin, soya hulls, agricultural and timber industry residues serve as raw materials for “naftaclean”. Substrate is crushed, then processed in dispersant, removed from the solution and dried. Then additives are produced for ferromagnetic particles. Finely disperse iron base powder FER-3, having a high level of coercive force (up to 30 кA/m), is spread on the spill film. It does not destroy the spill film of oil product but modifies its properties, which creates an opportunity to collect it by means of magnetic devices. The effectiveness of the method is sufficiently low because the modification process is slow, but the upward thrust is small.

In Riga Technical University, the work on creation of sorbents having ferromagnetic properties and their use in the development of technologies was started in the late 1990s. Simple sorbents from different types of iron powders, as well as fine-cut rolling mill scale were basically used [74], [75]. These sorbents have inherent range of substantial shortcomings. They have low buoyancy and low sorption capacity. These studies have mainly used iron base powder materials: iron powder ASC 100.29 (dusted one, used for the production of constructive components by means of powder metallurgy method), powder MH 80.23 (recombined porous one, for use in the manufacture of automatically lubricating slip bearings), and powder of M20/80-19 (with decreased carbon content) [79]. Powder coarseness is determined by its objective. Powders 40–100 are primarily used for the purpose of production of powder preparations, while powders in the micron and submicron range are used for the production of ferromagnetic suspensions [80]. Such powders are normally used for non-destructive control of the products of mechanical engineering and other sectors.

Magnetic properties of materials are largely determined by chemical composition and density of the substance. Efficiency of technological processes controlled by magnetic or electromagnetic fields is repeatedly dependent therefrom.

Studies have revealed a principled possibility for application of iron powders for sorption of different substances. In addition, it was established that effective use of the method requires resolving of very many tasks: to assess the sorbtion efficiency and to reduce the costs of sorbents, to increase their buoyancy by means of high-speed magnetic devices, to develop appliances for sorbent spraying and sludge collection.

1.5. Potential Components for Production of Composite Sorbents from Lightweight Materials

The main disadvantage of the iron containing ferromagnetic sorbent materials is their high specific weight, increased oxidizability, and low buoyancy. In this context, components from lightweight materials should be examined for manufacturing of composite sorbents. Attention should be paid to natural light materials such as fine-cut peat, sapropel, and sawdust. At the same time, during recent years products have appeared in the production, such as cenospheres, from technological residues and other ceramic materials.

Ceramic industry waste

The ceramic industry creates a lot of light easy dispersable technological waste when producing surfacing tiles, bricks, etc. [91]. Their bulk density ranges between 0.45 and 1.5 g/cm^3. It consists mainly of silica and aluminium oxides. Residues are used for various purposes. For example, certain batch material is used for the production of glass ceramics. It contains 30–60 % of residues from alunda abrasive circle processing in ceramic link (corundum) and 40–70 % of glass obtained by crushing the glass residues.

However, it should be noted that use of such residues in the status of sorbents and their components may cause certain difficulties in relation to the need to carefully define their chemical composition, sorting and pressing into granules. These materials can additionally contaminate the environment.

Aluminosilicate microspheres

The lightest component, which is formed at the same time with ash, is represented by aluminosilicate microspheres (MSPs), which tend to have extremely low bulk density (0.3–0.5 g/cm^3), and which are carried away by flue gases together with very fine light ash [93]. These

MSPs together with ashes are getting into ash sedimentation tanks, where, due to their low density they accumulate mainly on the sediment layer surface, and they can easily be taken away by rain and wind. The most dangerous possibility is spreading in the environment by wind, due to the fact that they can travel long distances and penetrate into human and animal respiratory tracts, promoting cardiovascular and respiratory diseases [94]. At the same time, however, MSPs have several unique characteristics, which prospectively make their efficient use in many modern technologies possible. It contributes to the need for improvement of their collection methods, to explore in depth their properties and creation mechanisms, as well as to develop the optimal methods of use [95]. There are two main categories of MSPs: "empty spheres" where the cavities are filled only by gas; so-called cenospheres (CS); and plerospheres (PS) where the cavities are filled with small mineral particles, foam, spongy or some other kind of porous structure. MSPs are created from amorphous, glass like material, which contains amorphous SiO_2 (50–65 weight%), Al_2O_3 (20–30 weight%), Fe_2O_3 (1–8 weight%), as well as Ca, Mg, etc., phosphates, sulphates, chlorides, as well as quartz, mullite, etc.

Appropriate assessments are usually obtained from studies regarding a partly broken MSP. CSP has a potential for their use in filters, various types of insulation, anti-corrosion coating, protection layers on a liquid surface in order to reduce evaporation, energy absorbing shock absorbers and other vehicle components, pneumatic tyres, et al. Properties of CSs and ashes are mainly determined by their chemical composition and texture (in this case, texture means the structure at supramolecular level). In some literature sources most of the attention is focused on chemical and phase composition.

Peat

Peat is one of the most important natural resources in Latvia. Total bog area in Latvia reaches 6401 km^2 or 9.9 % of its total territory.

Peat as a natural sorbent is known for quite a long time and is used in various filters for the purpose of decontamination from organic and oil containing products dissolved in water. Peat morohologic and chemical composition allows it to carry out mechanical decontamination on the account of fibrous structure, as well as biological and chemical decontamination. This makes it one of the most optimal and budgetary options for using it as a filter material in sewage treatment systems [98].

Sapropel

Sapropel is created at the bottom of freshwater reservoirs, mostly lakes, which do not have running water [101]. After acquiring, it is dried and becomes a powder, which later is pressed in granules or left in bulk. It should be noted that humidity of sapropel in original condition is up to 97 %. It quickly dries down to 55 % of humidity, then dries very slowly. Specific weight in the dried form reaches 1.4–1.7 g/cm^3. Granules are the most preferable to be used as sorbents (Fig. 1.4).

Fig. 1.3. Dried sapropel granules.

2. THEORETICAL PART

Previous studies in the field of sorbents with ferromagnetic properties indicate that it is necessary to further develop methodology for creation of effective sorbent with enhanced sorption and buoyancy, as well as to analyse its interaction with electromagnetic and magnetic systems. Furthermore, it is clear that effective sorbent must be a combined product consisting of several components.

2.1. Combined Ferromagnetic Sorbent Model

The new combined sorbent (*Comsor*) proposed by authors [102] is based on a hollow thin-walled microsphere 1, made of ceramic material (Fig. 2.1). It has low specific weight and good buoyancy. Its surface in the original form has a small specific surface. In addition, the microsphere itself usually does not possess magnetic properties. Therefore, by means of binder *2*, the surface of microsphere 1 is covered by powdered layer 3 of ferromagnetic particles. Overall effectiveness of such sorbent depends on the magnetic properties of these particles and the conglomerate. Flake-based particles of materials 5 can be applied on the microsphere surface, the task of which is to improve the adhesion with OP.

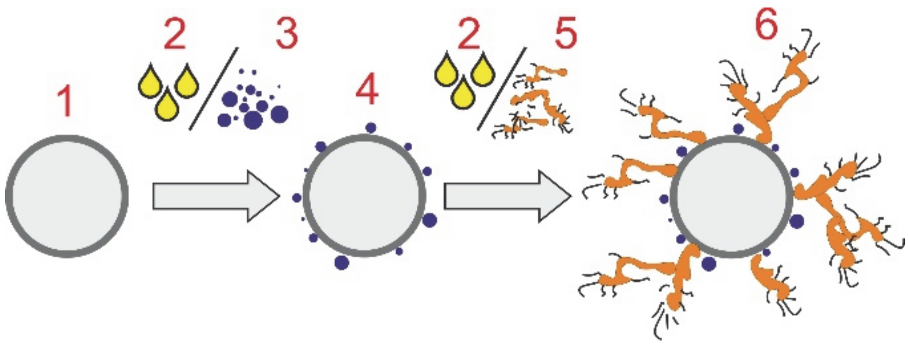


Fig. 2.1. Sorbent building phases:
1 – cenosphere; 2 – binder; 3 – ferruginous powder; 4 – CS *Comsor*;
5 – peat particles; 6 – CS *Comsor-125.*

OP sorption by means of microspheres is taking place in many processes [103]:

- OP adhesion with ferromagnetic particles by adhesion;
- OP mechanical grip with flake-based elements;
- OP holding between particles with capillary effect (Fig. 2.2).

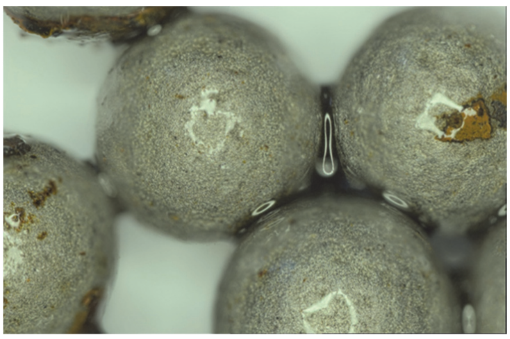


Fig. 2.2. Holding of OP in the cavities formed by the microspheres.

In this case, capillary effects are playing an important role (Fig. 2.3).

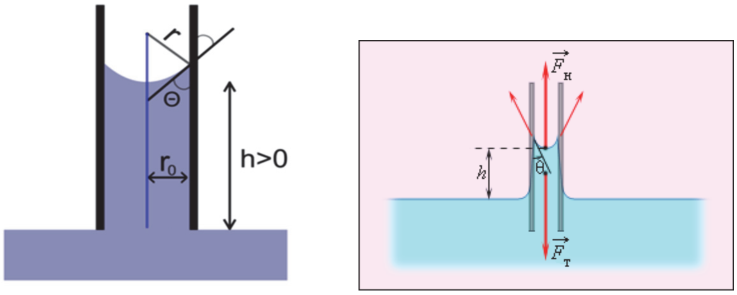


Fig. 2.3. Capillary phenomena scheme (a); and operation of forces in capillary (b).

The formula that determines the height of liquid rise in a capillary (Borelli-Jurin's formula) is described as

$$h = 2\sigma \cos\theta / r_0 (p - p_0) g, \quad (2.1)$$

where

- σ liquid surface tension coefficient;
- h lifting height of the liquid column;
- θ angle for moistening of the capillary wall with liquid;
- g free fall acceleration;
- p liquid density;
- p_0 gaseous phase density;
- r_0 capillary radius.

The smaller the capillary radius r_0, the higher the liquid rises. The height of a liquid column rise is increasing also with the growth of liquid surface tension coefficient. Liquid rise in the capillary continues until the module of gravity F_T acting on the liquid column in capillary is equal to the resulting surface tension F_H force module operating along the liquid contact border with the capillary surface.

Calculations were made for the following materials:

- ceramic microsphere having diameter of 100 µm, density of 0.4 g/cm^3;
- iron powder monolayer with particle size of 30 µm.

F_T – sludge gravity (Fig. 2.3 b) depends on the sorbent, OP, water mass, and specific gravity. In calculations the quantity of water can be accepted, which is being held at the microsphere pores to 5–8 %, but the oil absorbent capacity – up to 30 % of the sorbent weight.

2.2. Impact of the Magnetic Field on Fine-Dispersed Particles in Water

The method for water decontamination from OP by means of feromagnetic sorbents is based on interaction of the magnetic field with fine-dispersed particles possessing magnetic properties [106]. Iron and iron containing materials comprising nickel and cobalt are the most interesting. Under the impact of the magnetic field magnetization J is carried out in the magnetic material, characterised by material amount of magnetic moment M/V. Magnetization of magnetic material at certain intensity of known magnetic field tension H_E reaches the highest value J_E, which does not change at further increase of the field tension. This value is called a saturation magnetization. For iron it constitutes $1.27 \cdot 10^6$ A/m [107]. This can be achieved with large magnetic field induction values. For iron it constitutes approximately 2.15 T_L, but for nickel – only 0.61 T_L [108].

It should be stressed that the properties of magnetic materials such as, for example, saturation magnetization, magnetic permeability, magnetic energy, etc., mainly depend on the material crystalline structure. Therefore, the use of nickel containing steel waste as basis for the sorbent is preferred, but copper or phosphorus in the content of sorbent have no impact on the sorption process.

If electromagnetic field operates with tension H_1, magnetization of the material reaches its volume of J_n, but then changes depending on the relaxation time k.

$$J_n = J_\infty (1 - e^{-t/k}), \qquad (2.2)$$

where J_∞ is material magnetization at $t = \infty$; and k is relaxation time.

Technically pure iron is a magnetic material with the highest saturation magnetization. Therefore, it is the most preferable to be used for the sorbent manufacturing.

Another important parameter influencing sorption process of the ferromagnetic sorbent is its magnetic permeability μ. It indicates how many times the magnetic field induction in the environment B (that is, sorbent on OP surface) is different from the external magnetized field B_0.

It is high content of carbon, oxygen and sulphur, which reduces μ the most. Therefore, extended storage of a sorbent will cause its quality deterioration and reduction of its sorption efficiency. Use of steel with *high carbon content* as ferromagnetic sorbent is not practical as well.

Holding of sludge on the water-oil surface is taking place on the account of environmental surface tension forces (in this case, as water-oil film), as well as due to air pillow present in the sorbent particle pores. As the sludge rises due to the film surface carving, Fa value decreases. Fa value, in calculation of the required capacity of the magnet power, may be taken into account in the form of coefficient 1.1–1.2.

The upward thrust value of electromagnet Fm is determined by formula

$$F_m = 4\pi \left(\frac{nI\mu\alpha}{cL} \right)^2, \qquad (2.3)$$

where

- n number of the electromagnet windings;
- I current in winding;
- μ magnetic permeability of the environment;
- α magnetic thickness;
- L circuit perimeter;
- c the speed of light.

3. METHODOLOGICAL PART

3.1. Experimental Research Methodology, Methods and Equipment

Size of the particles was determined by means of the light microscopy method with the *Biolam 70*-R microscope. Investigation of the powder fraction composition was carried out with the device in accordance with methodology [109]. Fluidity of dry powders and mixtures was assessed according to methodology at the device, as shown in Fig. 3.1.

Scanning electron microscope (SEM) *Zeiss EVO MA*-15 with high resolution and the reflected electron detector (BSE) was used for examination of the particle surface morphology.

Experimental work was carried out with powdered materials having particle size between 10 and 200 µm. Therefore, a variety of equipment was used for examination of the properties of powders as such, and the produced mixtures, as well as sludge containing ferromagnetic powder, water and oil products. Properties such as the particle bulk weight, size and shape, fluidity of powdered materials, binding capacity in regard to oil products, water absorption, buoyancy, etc. was first established.

Fig. 3.1. Powder fluidity evaluation device.

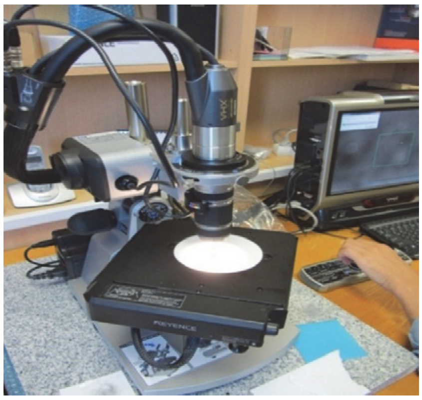


Fig. 3.2. Microscope VHX-2000: Keyence REMAX.

The volume meter was used in order to assess bulk weight [110]. Conical graduated plastic test-tube was weighed, the volume of which is 1.5 cm^3, it was placed in 1 cm^3 of the substances to be studied, and the weight of test-tube with the substance was determined. Bulk weight of the substance was calculated as the weight difference between the test-tube with the substance and the test-tube itself. Weighing has taken place on the *Ohaus* analytical balances with accuracy of measurement 0.1 mg, and secondary electron detector (SE) [111]. The black and white images have been obtained by means of computer and analyzed in the *Image Pro 7* image analysis system (*Media Cybernethics*) [112]. EDS, equipped with *INCA Energy* 350, was used to assess the CS morphology and structure.

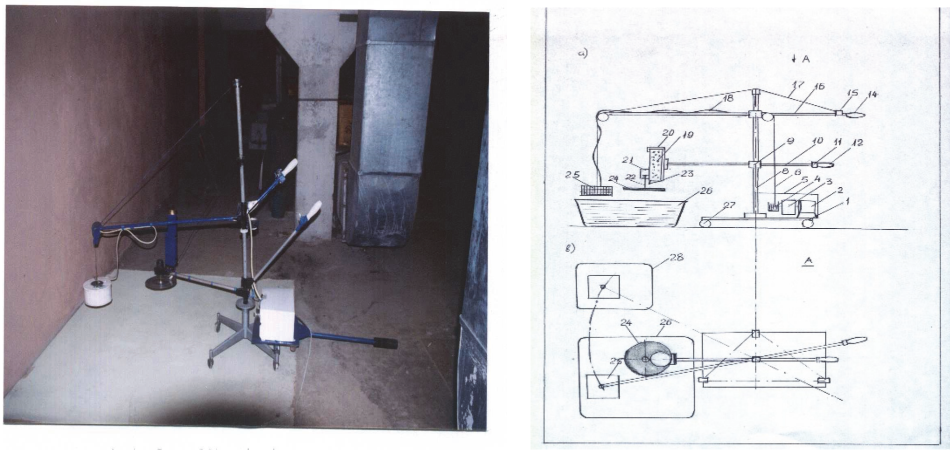
Surface of cryogenic fracture was used in order to capture the scanning electron micrographic. The *Keyence* corporation optical microscope VHX-2000 with VH-Z20R/W and VH-Z500R/W lenses was used for optical creation of images (Fig. 3.2) [113].

Thermal analysis equipment STA 449F1 *Jupiter* of firm "NETZSCH-Gerätebau GmbH" (Germany) [114] was used for *thermogravimetric research*.

XRD measurements were made using *Rigaku Ultima+* diffractometer with Cu Kα irradiation. Identification of the crystalline phase was implemented by means of the database of International Centre for Diffraction Data (ICDD) and *Sleve+2008* software [115].

Specific surface of the powders was determined by means of the "Beckman Coulter, Inc." (U.S.) analyser SA 3100 [125].

Powder spraying was carried out with the newly developed equipment [117] (Fig. 3.3).



a) b)

Fig. 3.3. Experimental device for spraying of powdered sorbent and for collecting sludge by means of electromagnet: (a) overview; and (b) scheme.

The device (Fig. 3.3) consists of mobile platform ***1***, where an electric motor ***2*** is installed with a reducer ***3*** and a winch ***4***. An electromagnet lifting drive ***25*** is covered with housing ***5***, electromagnet hanged up in a steel wire ***6***. A vertical stanchion ***8*** is also fitted on the platform ***1***, on which a horizontal bar ***10*** by means of a socket ***9*** is fixed with a powder spraying unit. The powder is placed in a tank ***19*** with ***23*** and cap ***20***, on the tank ***19*** wall electric motor ***21*** with spindle ***22*** and disk ***24*** is mounted. Electromagnet ***25*** rotation control is implemented with handle ***14*** located on the horizontal bar ***16***. The tank (Fig. 3.4 a)) capacity is 2 litres. By means of drive the disc ***24*** rotates at a speed of 2000 rpm, which allows to perform powder spraying with speed 2–2.5 m/min.

a) b) c)

Fig. 3.4. Experimental equipment units: a) spraying mechanism; b) bath; and c) electromagnetic coil for sludge lifting by means of flexible wire cable.

Electromagnet lowering to the water surface takes place via drive by electric motor. Movement of electromagnet in the horizontal plane of work area is taking place through lever ***16*** and handle ***15***. Flat type electromagnet is weighing 4 kg. It is twisted from the copper wire with a diameter of 1.2 mm. When delivering 4 A power supply to the winding, its carrying capacity reaches 0.3 kg, but at 6A power – 7.5 kg.

Crushing of the materials is used for *manufacturing of sorbents* with high speed disintegrator (12000 rev.$^{-1}$) [128], mixing powders and emulsion preparation by means of dispersant [116]. *Collection of the sorbent with captured OPs* is implemented by means of magnetic [118] and electromagnetic equipment [120], which was developed anew.

Determination of *water absorption of sorbents and raw materials* was carried out in accordance with the methodology in a plastic test-tube, the volume of which is 5 cm^3, 500 mg of the original substance and a sorbent was inserted, test-tubes weighed and 4 ml water added. Test-tubes containing the substance or the sorbent and water were placed in a mechanical shaker or incubated for 30 minutes. Water was drained from the test-tubes through thick paper filter and the test-tube weight was determined together with sorbent after contact with water. Calculations were made on the basis of water absorption ratio between the original material and the sorbent obtained on its basis.

The *sorbent binding capacity* in relation to oil products was established in accordance with the methodology [16]. The amount of 30 cm^3 of water and 1 cm^3 of oil was poured into a previously weighed Petri plastic container, the volume of which was 50 cm^3. Weight of sorbent as 50 mg or 100 mg was taken, and th sorbent was imposed from the top onto the oil slick, and mixed, by gently shaking for 5 minutes, and the collected mixture was removed from the surface. The completeness of removal was assessed either visually or by weighing.

Kinetic persistence in disperse systems (ability of a disperse system to retain uniform particle layout along the entire environmental capacity volume) is described by Stokes' law [129]:

$$V_S = \frac{2}{9}\frac{r^2 g(\rho_p - \rho_f)}{\mu}, \tag{3.1}$$

where

- V_s stabilised particle velocity (m/s) (particle moves downwards if $\rho_p > \rho_f$, and upwards if $\rho_p < \rho_f$);
- r Stokes' radius of the particle, m;
- g gravitational acceleration, m/s²;
- ρ_p density of the particles, kg/m³;
- ρ_f fluid density, kg/m³;
- μ fluid dynamic viscosity, Pa·s.

On the basis of Stokes' formula (3.2), sedimentation (segregation) speed is directly proportional to the speed of squared difference between the radius of particles, phase and the environmental density, as well as inversely proportional to the environmental viscosity.

The *volume occupied by inter-particle gaps* is calculated according to formula

$$\overset{total}{P} = \frac{V_{par}^{solut.}\,(V_{kop} - V_{\check{s}kid})}{V_{par}} \bullet 100\%, \tag{3.2}$$

where

- V_{par} is free bulk sample volume, ml;
- V_{total} is mixture (sample + liquid) volume, ml;
- V_{solut} is volume of the starch solution, ml.

Magnetization of the materials was taking place by means of magnetization device (Fig. 3.5). *Magnetization of the material* was evaluated by Gaussmeter (Fig. 3.6).

Fig 3.5. Magnetization device.

Fig. 3.6. Gauss/Tesla Meter FH-55, MAGNET-PHYSIK Dr. Steingroever GmbH.

3.2. Materials Used for the Research

Iron powders, shred metal particles of rolling mill scale and certain other metallurgical industry waste was used for manufacturing of the sorbents with feromagnetic properties as original powder-based materials. For example, the author has selected the following brands of metal powders: ASC 100.29 – sprayed, used in the manufacture of structural parts with powder metallurgy techniques; MH 80.23 – restored porous, used in the manufacture of self-lubricating plain shaft bearings; M20/80-19 with a low carbon content and R-12 with reduced hydrogen content used in the manufacture of friction products. All the powders are produced by the company *Höganäs AB* (Sweden) [79]. Powders, such as ПЖРВ [PZRV] were used as well, which were sprayed with air and produced by *ООО "ССМ-Тяжмаш"* [SSM-Tyazmash Ltd] (Russia) [126], ПЖР [PZR] 3.315.26 -30, sprayed with water and produced by КЗПМ [KZPM] (Ukraine) [127]. An opportunity to use RTUS-1 brand of rolling mill scale of Liepaja Metallurgical Plant as the sorbent was studied as well.

4. CREATION OF COMPOSITE FERROMAGNETIC SORBENT (EXPERIMENTAL PART)

When working on the topic "Ferromagnetic Sorbents and their Potential for Collecting Pollution with Spilled Oil Products", much attention was paid to experimental work, which covered the ferromagnetic sorbent manufacturing and operational phases, as well as their reuse and recovery capabilities.

Topicality of the creation of composite powdered ferromagnetic sorbent with typical KFMS magnetic properties is highlighted in many patent studies, especially in [131]–[133]. The authors have used different bases, which were saturated with fine-dispersed (ferromagnetic) particles. In this direction Riga Technical University has commenced the studies also with *fine-sprayed* iron powders [17]. Common disadvantage of the previous studies is high proportion of sorbent particles causing their poor buoyancy.

This Thesis offers a new technology for production of composite ferromagnetic sorbent (CFS) [134], which includes the preparation of hollow ceramic material cenosphere (CSP) base, then modifying thereof, by applying ferromagnetic powder and adding light products that increase buoyancy and sorption capacity.

This Thesis has studied commercially available ways of four cenospheres, their origin (field and thermoelectric power plant) shown in Table 4.1.

Table 4.1

Designation, Source of Origin and Granulometry of the Used CSF

Sample description	***Coal deposit***	***TPP***	***Granulometry, µm***
CSF1	Kuznetskoe	Troitskaya	250−500
CSF2	Kuznetskoe	Troitskaya	56–100
CSF3	Kuznetskoe	Troitskaya	150–250
CSF4	Ekibastuz	Tomusinskaya	0–500

As you can see, the samples CSF1-CSF3 have come from the same coal deposit and TPP, where CSF is formed in the carbon incineration process, only the granulometric composition and the delivery price differs. However, several characteristics must be determined, because incineration modes may vary, there may also be inaccuracies in the raw material data provided by the supplier.

As it has already been stated in the theoretical part of the paper – cenospheres are hollow, spherical objects with a smooth surface. Cenospheres, which were used in this Thesis, also have the above mentioned properties clearly visible in the images obtained with optical (Fig. 4.1) and SEM microscope (Fig. 4.2).

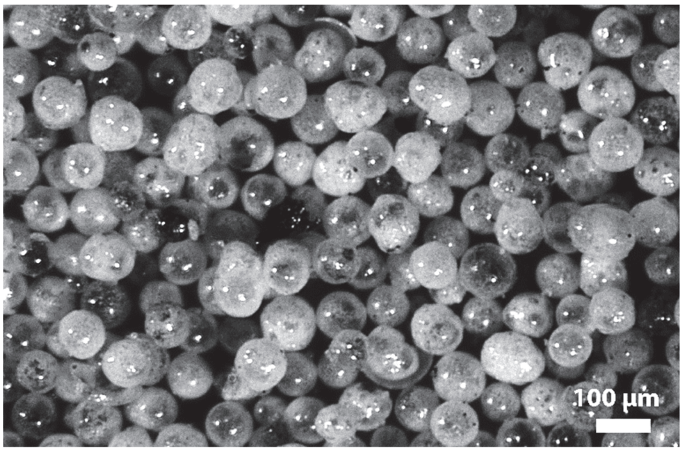
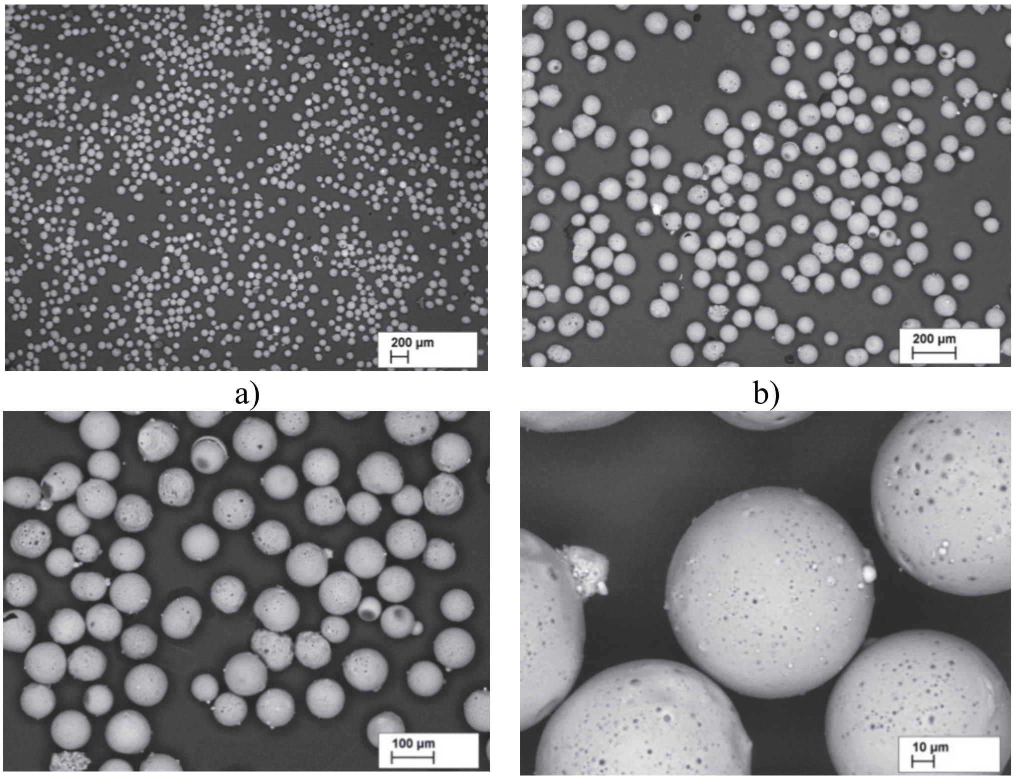


Fig. 4.1. Sample photomicrography obtained with optical microscope CSF2.

More than 15 optical microscopy images were made for each sample. The most typical of those are shown in Fig. 4.2. Upon their analysis it can be concluded that almost all particles of sample CSF2 have a correct spherical shape practically free of inclusions, their appearance is homogeneous, unlike of the samples CSF1, CSF3 and CSF4.



a) b) c) d)

Fig. 4.2. SEM images of CSF2 microsphere with enlargement of a) 20x; b) 50x; c) 100x; and d) 500x .

Sample CS1 presents objects, which have very different transparency and colour – they have transparent, semi-transparent, and opaque (white) cenospheres. The degree of transparency is likely dependent on the cenosphere wall thickness and its construction. Sample CSF3 has typical black inclusions (possibly incompletely burnt coal). Small balls CSF4 were found in the sample with size more than 500 µm, which was later confirmed in granulometry analysis.

Composite sorbent (KS) was made in a special mixer – reaction chamber (Fig. 4.3). Continuous rotation of an obliquely installed cylinder was taking place with a speed of 300–500 rpm.

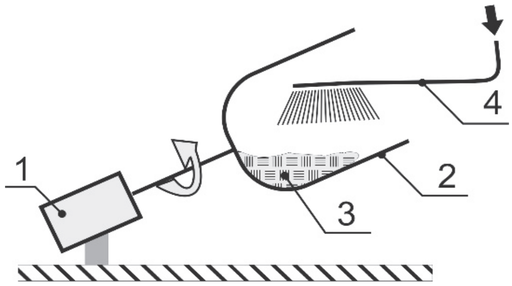


Fig. 4.3. Scheme of installation of KS production:
1– motor, 2 – cylinder, 3 – material to be processed, 4 – binder delivery.

Microspheres, particles of ferromagnetic material, components increasing the specific surface (for example, aluminium flakes and / or peat particles) are supplied in certain proportions to the reaction chamber (rotating cylinder). During collision of binders, as well as during further ball production process, the particles mutually agglutinate, creating KS. Binder hardening is attained through heating. Separation of the finished product is further performed from raw material components with magnet and gravity separators. In addition, the sorbent may be treated with hydrofobising composition.

Composite sorbents *Comsor, Comsor-125,* and *Comsor-M* are developed in cooperation between Riga Technical University and Rezekne Academy of Technologies. The technology of obtaining is described in Patent P-12-205 on 28 December 2012 [2] .

The scheme of the KFS manufacturing process is shown in Fig. 4.4.

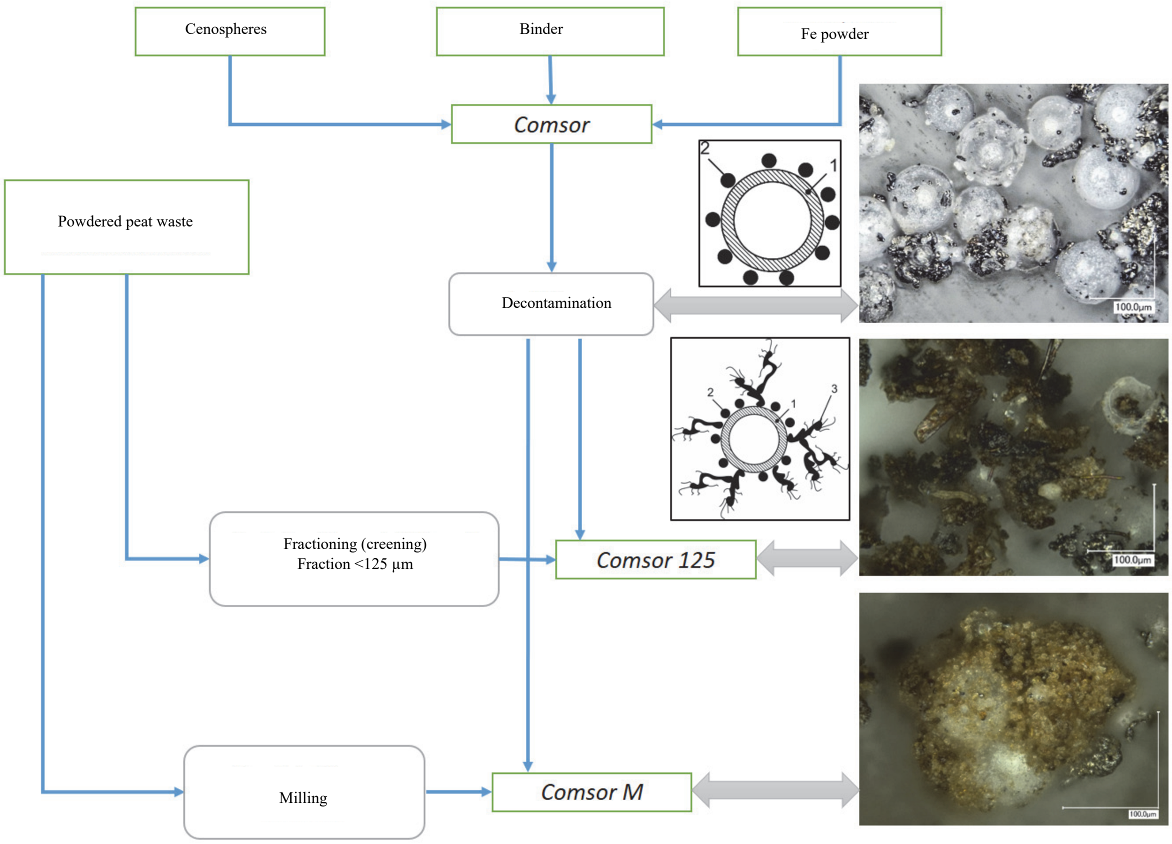
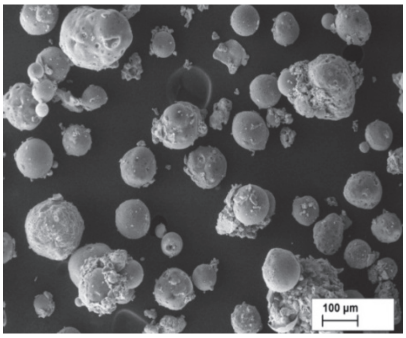


Fig. 4.4. The scheme for obtaining composite sorbent *Comsor, Comsor-125, Comsor-M*, and KFS Comsor morphology with varied enlargement.

KFS microstructure is displayed in Fig. 4.5.



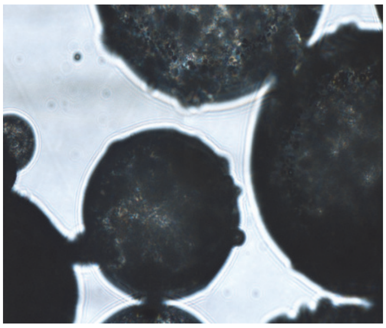


Fig. 4.5. KFS Comsor with varied enlargement.

Heating contributes to the binder hardening. Separation of the finished product from raw material components is carried out with a magnet and gravity separators.

KFS *Comsor-125* is made of KFS *Comsor*, for maximizing specific surface of the component, peat particles are used having passed through 125 μ large apertures.

KFS *Comsor-M* is produced in a similar manner. Maximising component of its specific surface – peat particles, ground in ball mills, are fed to the reactor chamber in certain proportions.

Oil sorption test results for the obtained KFS are as follows: *Comsor* – 1.32±0.12; *Comsor-125* – 1.87±0.18; *Comsor-M* – 1.53±0.11 (g/g). These data are well correlated with the particle morphology in accordance with the experimental data, according to which it is determined.

Comsor-125 can receive for 42 weight% and *Comsor-M* – for 16 weight% more oil than *Comsor*. Upon the analysis of sorbent activity, it is possible to claim that oil / petroleum is staying in the improved / enhanced / developed CFSs due to two reasons:

1) owing to peat particles with increased specific surface area of the sorbents;
2) due to filling of gaps between the sorbent particles.

Large increase in oil absorption for *Comsor-125* absorbent may be explained by hypothesis. Spherical objects in ideal circumstances may be arranged in four structural ways. The following arrangements may have different channels between particles that can be filled by liquids in the case of good moistening capacity.

5. NOVELTY OF THE THESIS

Scientific novelty of the Thesis

- New methodology developed for creation of new types of sorbents with ferromagnetic properties for sorption of oil products.
- A process model proposed for sorption of oil product films from water surface by means of ferromagnetic particles.
- Analysis provided regarding the impact of composition and properties of ferromagnetic sorbents on the sorption process.
- New methods offered for production of composite sorbents with ferromagnetic properties.
- New methods proposed for sorbent spraying and sludge removal from water by means of magnetic and electromagnetic devices.
- Data obtained for thermogravimetrical and differential thermal analysis of iron powder-base sorbent and the collected sludge in the temperature range up to 1000 degrees.
- Proposal for use of the collected OPS (oil product sludge) as high temperature fuel product.

Practical novelty of the research

- Some new composite sorbents (*Comsor 125*, *Comsor M,* etc.) developed with magnetic properties.
- New types of ferromagnetic sorbents developed on the basis of use of technological residues and natural raw materials.
- Stands developed, designed and tested for spraying sorbents on the water surface contaminated with oil products for study of the processes.
- Stands developed, designed and tested for collection of the sludge by means of magnetic and electromagnetic equipment.
- New sorbent recovery and reuse technology proposed.
- New ways for the use of sludge proposed, sorbents obtained with oil products (for concrete cutting with gas flame, production of fuel emulsions and copper extraction from solutions).

6. CONCLUSIONS

1. Upon examination of various methods and technologies to treat oil spills in the water by means of different sorbents, it was concluded that the powdered ferromagnetic sorbents (PFSs) are prospectively usable, which is explained by their non-toxicity, the possibility to apply new, rapidly developing treatment methods by means of magnetic fields, and recovery capabilities, as well as effective disposal techniques. Moreover, the PFSs were still little explored until now.
2. New types of composite ferromagnetic sorbents (*Comsor*) have been developed, which are based on the use of hollow microspheres (cenospheres) to surface of which ferromagnetic particles and extended fibres are attached. *Comsor* KPSs, in comparison with other iron powder-based FMSs, have shown their sorption increase by 5–7 %, while for buoyancy – more than ten times.
3. Iron powder crushing technology has been applied to production of KPS fine ferromagnetic particles by means of high speed impact action disintegrator. The selective crushing method has proved to be the most effective one.
4. A method has been developed for treatment of water from oils by means of electromagnetic device. The required dependence of the field voltage from the height of placement of the device above the polluted surface has been established. Use of the electromagnetic device has been demonstrated for lifting of sludge up from 1 m in depth.
5. The improvement potential of FMSs has been shown by means of processing and subsequent drying of the sorbent. It is also reasonable to assume that the sorbent can be reused. In addition, high speed impact action disintegrator was first used in the manufacture of ferromagnetic emulsions.
6. Sorption processes have been analysed by means of FMSs. The effect of shape and size of the particles is indicated. It has been determined that powders with a particle size of 20–40 μm with enlarged specific surface can be used in the most efficient way.
7. Sludge thermogravimetric research in the temperature range from 20 to 1000 °C has allowed to clarify certain important stages – below 150 °C, intense surface evaporation of water from the surface of iron particles is taking place, above 300 °C – evaporation of water from the particle capillaries. At the beginning the weight of powder decreases, however, the oxidation process results in almost 40 % increase. Sorption capacity of a sorbent together with oil amounts to 8 % of water on average. Sorption capacity of metal powder is amounting to 20–22 % on average. Processing of the used sorbents requires temperature of not less than 600 °C. Safe products H_2O, CO^2 are released during processing.

8. The technology has been developed and tested using the mill scale and the collected FMS for cutting of concrete.
9. Technology and equipment has been developed by means of the mill scale with FMS, for copper extraction from the solution.
10. Innovativeness of the research has been approved by two Latvian patents (see Annex).

ABBREVIATIONS AND SYMBOLS USED IN THE THESIS

OP – oil product
SOP– spilled oil product
MRM – metallurgical residual materials
MRCC – liquidation of the consequences of oil accidents
OPC – oil pollution case
FSS – fuel service station
FS – ferromagnetic sorbent
CS – composite sorbent
DS – hollow sphere
MSp – minisphere
McSp – microsphere
PU – polyurethane
PS – polystyrene
PVC – polyvinyl chloride
Bd – bulk density
SEM – scanning electron microscope
OM – optical microscope
LAD – high speed disintegrator
PIE – powder spraying equipment
XPS – X-ray photoelectronic spectroscopy
AFM – atomic force microscopy
TGP – thermogravimetry studies
DTA – differential thermal analysis
Ab – absorption
Ad – adsorption
γ – surface energy

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APPENDICES

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PATENTS

Latvijas Republikas Patentu valde apliecina, ka šajā patentā ietvertais izgudrojums ir iekļauts patentu reģistrā ar

Nr. 14822

Patents ir spēkā Latvijas Republikā 20 gadu no 28.12.2012., ja šis termiņš Patentu likumā paredzētajā gadījumā nebeidzas agrāk

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Patentu valdes direktors S. Laganovskis

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Patentu valdes direktors S. Laganovskis