Application of Regulations Concerning the Transport of Dangerous Goods Transported in Bulk

Marzenna Popek
Gdynia Maritime University,
Department of Chemistry and Industrial Commodity Science
marzenap@am.gdynia.pl

Abstract: The main task of International Maritime Organization and Governments is develop a comprehensive body of international conventions, codes and recommendations. Certain IMO activities are dictated by the need to take action on specific areas of maritime safety, and protection of marine environment: evaluation of safety and environmental hazards of chemicals, analysis of maritime casualties and maritime incidents reporting. When the wet granular materials, such as mineral concentrates and coals lose their shear strength, resulted from increase pore pressure, they flow like fluids. This phenomenon is called liquefaction and causes dangerous cargo shift. The main factor which influences on the liquefaction of solid bulk cargoes is moisture content. According to the chapter VI of the SOLAS Convention, it is required that cargoes which may liquefy shall only be accepted for loading when the actual moisture content of the cargo is less than its Transportable Moisture Content. In this work the results of investigation on possibility of using biodegradable materials as absorbers of water from mineral concentrates, before the transportation by sea, are presented. To prevent sliding and shifting of ore concentrates in storage starch materials are added to the ore concentrates.
Keywords: mineral concentrates, liquefaction, shifting, starch polymer

1. INTRODUCTION

International Maritime Organization and Governments should have the possibility to establish permanent arrangements in order to ensure the safe transportation of dangerous goods. The successful application of regulations concerning the transport of dangerous goods is greatly depend on the appreciation by all persons concerned of the risks involved and on a detailed understanding of the regulations. The International Maritime Organization plays an important role in the promotion of maritime safety and the prevention of marine pollution from ships. To have the greatest effect on safety of life, prevention of serious injury, protection of the marine environment the following items are taken into account as higher priority: measures to promote the widest possible implementation and enforcement of IMO instruments by the shipping community, measures aimed at substantially preventing maritime casualties or marine pollution incidents, measures following a series of incidents causing or indicating risk of loss of life, significant injuries to persons, measures aimed at improving the safety and health of ship's crews and personnel, measures to correct significant inadequacies identified in existing instruments.

1.1 IMO instruments for ensure safety transportation

The main task of IMO is to develop a comprehensive body of international conventions, codes and recommendations. The most important conventions are accepted and implemented by countries whose combined merchant fleets represent 98% of the world. The International Maritime Organization has adopted over the years a number of internationally recognized codes and guides, which are of direct relevance to the safe and secure transport and handling of dangerous cargoes in port areas, and which may serve as valuable source of information in the development of national legal requirements

Some goods transported by sea can present a hazard during transport because of their chemical nature. The term "dangerous goods" includes any empty uncleanness packaging (such as tank-containers, receptacles, intermediate bulk containers (IBC's), bulk packaging, portable tanks or tank vehicles) which previously contained dangerous goods, unless the packaging have been sufficiently cleaned of residue of the dangerous cargoes and purged of vapors so as to nullify any hazard or has been filled with a substances not classified as being dangerous. The classification of dangerous goods and general provisions concerning listing, labeling were adopted in 1948.

The International Convention for the Safety of Life at Sea (SOLAS Convention) is the most important international convention dealing with maritime safety [1]. SOLAS in a present version was adopted in 1974 and entered in force in 1980. The provisions of Chapter VII of the Convention "*Carriage of dangerous goods in packed form or in solid form in bulk*" contain the main regulations concerning the transport the dangerous goods by sea. To minimizing the risk of negligent or incidental release of marine pollutants transported by sea The International Convention for the Prevention of Pollution from ships (MARPOL 73/78) was adopted and entered into force on 2 October 1983 [2].

As a further step to regulate the carriage of dangerous goods by sea was approval by Maritime Safety Committee the International Maritime Dangerous Goods (IMDG Code) in 1965 [3]. The IMDG Code amplifies the requirements of both conventions and has become the authoritative text on all aspects of handling packed dangerous goods and marine pollutants by sea. Since 1 January 2004, the IMDG Code has attained mandatory status. To ensure safety sea transport of solid bulk cargoes the Sub-committee on Containers and Solid Bulk Cargoes (DSC) of International Maritime Organization (IMO) issued International Maritime Solid Bulk Cargoes Code (IMSBC Code) [4].

1.2 Mineral concentrates – MHB cargoes

Bulk shipping has been used for many years to reduce the cost of sea transport and the transport of bulk cargoes is a vitual component of international trade. Such trade require a sufficient volume of cargo suitable for bulk handling and hence justify a tailored shipping operation. The five major dry bulk cargoes are coal, mineral concentrates, grain, bauxite and phosphate rock, and each year the trade in bulk increases [5].

The safe transportation of solid bulk cargoes is a responsible task. Some of these cargoes are classified as dangerous goods - Materials Hazardous in Bulk (MHB). Shipment of solid bulk cargoes may be associated with several hazards. One of these hazards is deterioration or loss of ships stability, which may be a result of lateral shift of an excessively wet loose cargo, which can pass into liquid state.

The ore concentrates and similar materials are considered as a three-phase structure, which consist of: solids (mineral grains), water and air. Mineral grains are very small; they are from 0,001 mm to several millimetres large. Disintegration level and percentage of particular size fraction may differ depending on concentrate type.

In three – phase structure air and water fill the pores between mineral grains. When the cyclic load is applied to such material in sea transport conditions, due to ship rolling and vibration, particles of a material may move microscopically and the volume of void may decrease. The air, permeability coefficient of that is about 500 times greater than that of water, first escapes. In such case, if the void is filled with the water and the water flow through the small void is resisted, the pressure of the water in void increases. Shear strength of granular materials is maintained by friction force between particles and cohesion. Friction force is a product of effective compressive force between particles and a friction coefficient. When pressure of water in void become high, effective compressive force between particles become small. In such cases, if the cohesion is negligible, shear strength of the granular material becomes very low and the material flows [6,7]. Such phenomenon is called *"liquefaction*".

The main factor which influences on the liquefaction of solid bulk cargoes is moisture content The basic idea of the requirement for the material which may liquefy is limitation the moisture content of the cargo. To minimize the risk of liquefaction the IMSBC Code introduces the upper bound of moisture content of cargo, which is defined by the Flow Moisture Point (FMP). Flow Moisture Point is moisture content, which allows for passing the bulk cargoes from solid into liquid state. For materials prone to liquefaction, the IMSBC Code provisions is that cargo must be shipped at moisture content significantly less than the FMP. According to the chapter VI of the SOLAS Convention, it is required that cargoes which may liquefy shall only be accepted for loading when the actual moisture content of the cargo is less than its Transportable Moisture Content. The TML is defined as 90 % of the FMP. These cargoes prone to liquefaction, should never be carried without checking the moisture content. The IMSBC Code lays down that a certificate stating the relevant characteristics of the material to be loaded should be provided at the loading port, incorporating also the TML. The Code provides information how the moisture content of mineral concentrates can be tested and assessed. experimental procedures.

The behavior of a mineral concentrate that liable to liquefy and its threat to the ship's stability is closely related to the effect of a liquid free surface. Although this view may suitable in many cases, it does no fully reflect the known mechanisms of liquefaction. At a moisture content above that of TML, shift of cargo may occur as a result of liquefaction. Certain cargoes are susceptible to rapid moisture migration and may develop a dangerous base during the voyage, even if the average moisture content is less than the TML. Moist mineral concentrate, being compacted in the bottom layers and thus filling the gaps between particles completely with water, may slide on this saturated layer. The top layer may still appear in a dry and safe condition.

Both sliding and liquefaction are very dangerous: either may cause severe structural damage to a ship and both are known to have caused the loss of vessels carrying solid bulk cargoes. The events may take place gradually, giving a ship's master time to compensate for a shift in cargo or they may occur so rapidly that there is insufficient time to send off a distress signal before the vessel and crew are lost.

A large group of organic polymers fined use in the mineral industry with the specific function [8]. Particularly attractive are the new materials based on natural renewable resources, preventing further impact on the environment.

Starch is non – expensive biopolymer available from annually renewable resource. It is totally biodegradable in a wide variety of environments and allows the development of totally degradable products. The purpose of this work was investigation on possibility of using biodegradable thermoplastic materials as absorbers moisture. To prevent sliding and shifting of ore concentrates in storage materials composed of starch, cellulose and polycaprolactone are added to the concentrates.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Following concentrate was used for the test:

Flotation lead concentrate, composed mainly of PbS. The concentrate is produced in Ore Mining and Smelting Works in Trzebinia. Flotation lead concentrate is produced in a flotation process with the use of flotation and foam generating chemicals.

The water content in flotation lead concentrate is about 3,5 – 5 %. Flotation lead concentrate is a typical material, "which may liquefy".

Following starch materials were tested (potato starch obtained from Potato Industry Company at Luboń):

- Polymer Y Class – made of thermoplastic starch and cellulose derivatives from natural origin (made by Novamont S.P.A.),
- Polymer Z Class – made of starch and polycaprolactone (made by Novamont S.P.A.),
- Crosslinked starch – acetylic diamylaceus adipate -"Lubostat", (obtained from Potato Industry Company at Luboń),
- Crosslinked starch - diamylaceus adipate -"AD", (obtained from Potato Industry Company at Luboń,)
- Natural starch – granulated product, (obtained from Potato Industry Company at Luboń).

The samples of starch materials were in granular form. The experiments were conducted for samples of concentrate: without starch materials and for mixtures contain concentrate and 0,5%, 1 % and 2% of starch materials .

The used polymer materials are classified as a low environmental impact product.

The liquefaction may take place when the content of grains with the size 0,3 mm and less is grater then 10%. In the flotation lead concentrate the contents of particles with a diameter smaller than 0,3 mm are essentially greater than 10% and amount 62%.The content of particles greater than 1 mm is about 10%. This is the reason why flotation lead concentrates may liquefy.

The starch material does not significantly change grain size distribution of concentrates [9].

2.2 Methods

Estimation of FMP

The evaluation of FMP was performed with the use of the Flow Table Method and Proctor C/Fagerberg, according to the recommendations given in Appendix D in the IMSBC Code. Flow Table Method is not applicable for the coarse–grained concentrate, such as sedimentary galena. Application of this method is not possible if content of particles with size within 0,02 and 0,3 mm is greater than 10 %.

Permeability of concentrates:

The permeability is the rate at which water under pressure can diffuse through the voids in the mineral concentrates. Mineral concentrates are permeable to water because the voids between the particles are interconnected. The degree of permeability is characterized by the permeability coefficient k, also referred to as hydraulic conductivity.

According to the classification of soils, based on their coefficient of permeability, mineral concentrates are the materials with the low degree of permeability.The permeability of mineral concentrates depends primarily on the size and shape of grains, shape and arrangement of voids, void ratio, degree of saturation, and temperature.

Measurement of the cohesion:

The estimation of cohesion angle was performed in the direct shear apparatus by carrying the shearing with the help of lower and upper part of displacing box containing the tested concentrate. In the experiment the samples were compacted in a dry state. The moisture content corresponds to the TML value estimated in Flow Table Test.

In the experiments the samples were compacted. The consolidation conditions (in the holds) were simulated by using vertical loads: 0 N, 98 N, 196 N, 294 N and 490 N, what corresponds to the normal stresses: 0, 1,532 $*10^4$ N/m^2, 3,0645 $*10^4$ N/m^2, 4,589 $*10^4$ N/m^2, 7,659 $*10^4$ N/m^2 respectively. The test without any stress corresponds to the stress in the hold during the loading. Increasing values of normal stresses represents the changes in the bulk cargoes during the sea transportation.

3. RESULTS AND DISSCUSION

The value of TML for flotation lead concentrate is 7,4 %. The starch materials were added to the concentrates in wet state (water content corresponding to the TML of tested materials).

The results of estimation TML for mixtures of flotation lead concentrate with polymer Y and Z are presented in Table 1.

Table 1. TML values determined by means of Flow Table and Proctor C/Fagerberg

Samples	TML [%]	
	Flow Table	**Proctor C/Fagerberg**
Flotation lead concentrate	7,41	7,94
Flotation lead concentrate + 0,5 % polymer Y	7,42	7,98
Flotation lead concentrate+ 2,0 % polymer Y	7,5	7,85
Flotation lead concentrate+ 0,5 % polymer Z	7,35	7,82
Flotation lead concentrate+ 0,5 % polymer Z	7,4	7,91

Despite the presence of polymer in tested concentrates, the values of estimated TML are similar, because liquefaction is tightly related to the grain size contents. The results of the grain size analysis indicate that polymer does not significantly change grain size distribution. Results obtained by using ProctorC/Fagerberg Method are higher in all cases than those given by Flow Table Method.

The samples with Lubostat, AD and granulated starch were tested for estimation TML at several time intervals. The results are presented in Table 2 -3.

Table 2. Transportable Moisture Limit determined by Flow Table Method–flotation lead concentrate + 0,5 % starch

Sample type	**TML [%]**			
	Time			
	24 h	**48 h**	**72 h**	**96 h**
Flotation lead concentrate + Lubostat	8,11	8,6	8,8	8,8
Flotation lead concentrate + AD	8,8	8,9	8,9	9,0
Flotation lead concentrate + granulated starch	7,9	7,9	7,9	7,9

Table 3. Transportable Moisture Limit determined by Flow Table Method–flotation lead concentrate + 2 % starch

Sample type	**TML [%]**			
	Time			
	24 h	**48 h**	**72 h**	**96 h**
Flotation lead concentrate + Lubostast	9,40	9,45	9,5	9,45
Flotation lead concentrate + AD	9,35	9,33	9,36	9,39
Flotation lead concentrate + granulated starch	8,2	8,8	8,55	8,55

0,5 % and 2 % of starch material in mixture with flotation lead concentrate does not significantly change grain size distribution.

Starch material absorbed water from the mixtures at the amount approximately proportional to the starch material content in the mineral concentrates. It can be noticed that modified starch presents higher solubility than granulated starch. In general, the higher values of TML were observed in case of testing flotation lead concentrate + 2 % of starch material. For the mixtures containing 2 % Lubostat and AD the greater increasing of TML was observed than for concentrate containing 2 % granulated starch. The time of saturation of the starch material with water did not influence on the TML value.

The results of permeability tests are presented in Table 4.

Table 4. Results of permeability test

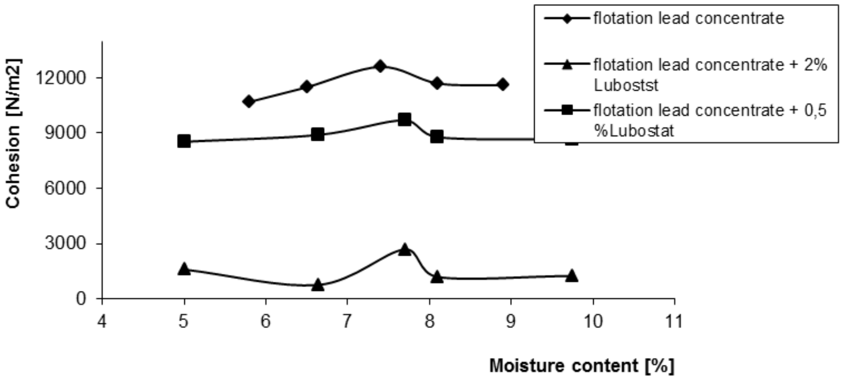
Sample type	Permeability coefficient [m/s]	
	Flotation lead concentrate + 1% of starch material	**Flotation lead concentrate + 2% of starch material**
Flotation lead concentrate + polymer Y	$2,2 *10^{-3}$	$1,35*10^{-4}$
Flotation lead concentrate + polymer Z	$3,5*10^{-3}$	$2,62*10^{-3}$
Flotation lead concentrate + Lubostat	$1,8 *10^{-3}$	$5,58*10^{-4}$
Flotation lead concentrate + AD	$2,34*10^{-3}$	$3,84*10^{-3}$
Flotation lead concentrate + granulated starch	$1,12*10^{-3}$	$2,33*10^{-3}$

Based on the results of the tests the effect of different content of the samples on the permeability was observed.

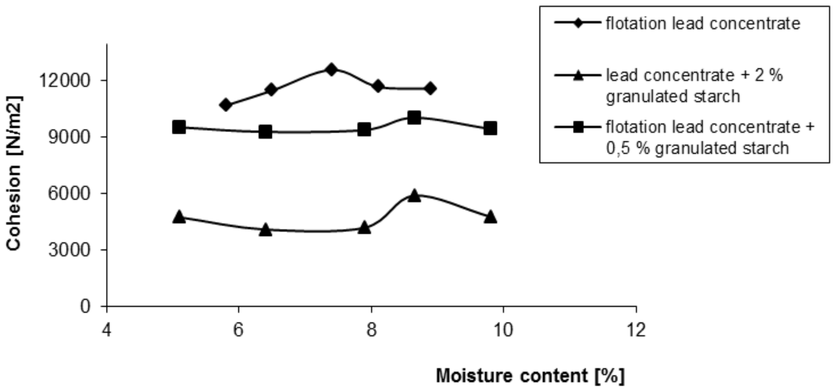
The maximum value of permeability coefficient k was achieved for mineral concentrate without any starch materials and reached the value $8*10^{-3}$ m/s.

The ability to permeability of mixtures is related to the type of starch material. In all cases, for samples with starch material, the decrease of permeability was obtained. If the content of starch material in the mineral concentrate increases, the value of permeability coefficient decreases. The greatest decreasing of permeability coefficient was observed for mixtures containing 2 % of Lubostat.

The changes of cohesion as a function of moisture content are presented in Figures 1 [a,b,c].



a]



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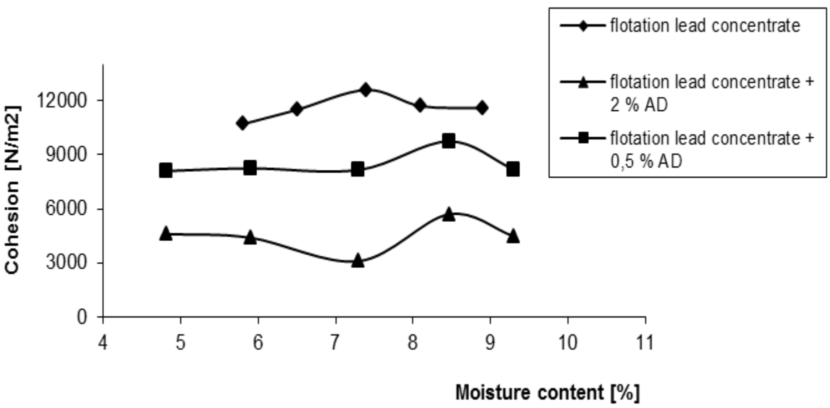

c]

Figure. 1. The changes of cohesion as a function of moisture content: a) flotation lead concentrate + Lubostat; b) flotation lead concentrate+ granulated starch; c) flotation lead concentrate+ AD.

The above presented results indicate that the starch materials significantly change the cohesion. Presence the starch materials in mineral concentrate tends to reduction of cohesion. In all tested samples cohesion increase with the increasing of moisture content and reaches a maximum with the moisture approaching the TML and then it goes down. The extreme values are not reached at the same moisture content for all mixtures. The maximum values of cohesion is effected by the type of mixture. It confirms correlations between the TML values and maximum values of cohesion.

4. SUMMARY

The conclusion is based on the measurement of the TML, cohesion and permeability of the materials.

The presence of starch materials in tested mineral concentrate influences on the value of the cohesion, and on achieving the maximum values. The comparison of the cohesion confirms that the correlation occurs between those values and the TML values.

In all cases, for samples with starch material, the decrease of permeability was obtained. The ability to absorption water is related primarily to the composition of starch material and the percentage of starch in mixtures. Due to presence starch materials the risk of its passing into the liquid state is lower.

Polymer materials prevent drainage of the water from the particle pore, sliding and shifting of ore concentrates in storage. These polymer materials can be used as absorbers of water from mineral concentrates.

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