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THE TRANSPORT STABILITY OF FLOTATION METAL ORE CONCENTRATES WHICH ARE LIABLE TO LIQUEFACTION

BEZPIECZEŃSTWO TRANSPORTU FLOTACYJNYCH KONCENTRATÓW RUD METALI ZDOLNYCH DO UPŁYNNIANIA

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Abstract: Safety of maritime transport of fine-grained materials, e.g. metal ore concentrates depends on the ability to control the properties of these cargoes. The dynamic situation, caused by vibration and pressure of layers of cargo during sea transport, makes it change its physical properties, porosity, bulk density, degree of compaction and mechanical properties, for example shear strength. The new properties of the cargo result in that there is a risk of its movement, as a consequence of the phenomenon of the liquefaction. In the present study were analysed and evaluated parameters that determine the ability to liquefaction of flotation metal ore concentrates characterized by different way of sourcing, chemical composition and fragmentation.

Keywords: mineral concentrates, stability, liquefaction.

Streszczenie: Bezpieczeństwo transportu morskiego materiałów drobnocząstkowych, np. koncentratów rud metali, zależy od możliwości kontroli właściwości tych ładunków. Dynamiczna sytuacja, wywołana wibracjami i naciskiem warstw ładunku podczas transportu morskiego powoduje, że zmieniają się jego właściwości fizyczne, porowatość, gęstość objętościowa, stopień zagęszczania oraz właściwości mechaniczne, np. wytrzymałość na ścinanie. Nowe właściwości ładunku powodują, że pojawia się zagrożenie jego przemiesz-czania się, będące wynikiem zjawiska upłynniania. Na skutek przesuwania się nadmiernie zawilgoconego i rozdrobnionego koncentratu, wywołanego upłynnianiem, może nastąpić obniżenie lub utrata stateczności statku. Istnieje zatem konieczność prowadzenia ciągłych badań nad poprawą jakości ładunków masowych i bezpieczeństwa ich transportu morskiego. W prezentowanej pracy przeanalizowano i oceniono parametry decydujące o zdolności do upłynniania koncentratów flotacyjnych rud metali, charakteryzujących się różnym sposobem pozyskiwania, składem chemicznym oraz rozdrobnieniem.

Słowa kluczowe: koncentraty rud metali, stateczność, upłynnianie.

1. INTRODUCTION

International sea transport moves about 90% of global trades (cargoes and commodities) to communities all over the world. Shipping is the most efficient and effective method of international transportation of goods when compared with the volume of the goods being shipped. Maritime transport is indispensable in a sustainable global economy as it is the most environmentally sound mode of mass transport, both in terms of energy efficiency and the prevention of pollution. In the past three decades, the volume of sea transportation grew by about 3,1% per year.

United Nations Conference on Trade and Development, making an annual analysis of the maritime economy, divided all the cargoes according to the following groups:

- oil and oil products,
- dry cargo, divided into two groups:
 - 1) five basic solid bulk cargoes: concentrates and iron ore, coal, bauxite, phosphates, and grain,
 - 2) other bulk cargoes: metal ore concentrates, agricultural goods and construction materials.

The volume of cargo transportation of these groups is an indicator of the global economy [UNCTAD 2014]. Solid bulk cargoes belong to two major groups of goods classified in maritime transport.

The growing supply of dry bulk tonnage suggests that the share of major dry bulk volumes still increases. About 28% of total seaborne trade were contributable to iron ore, coal and grain.

Carrying solid bulk cargoes involves serious risks, which include reduced ship stability and capsizing due to cargo liquefaction, chemical hazard (fire, explosion, toxicity) and damage to ship structure.

International Maritime Organization is focused on establishing the fundamental regulation that will need to be in place and applied in order to ensure that the world transportation continuous to develop safety (sustainably).

The transport of solid bulk cargoes is a subject to rules, which are based on internationally applicable commercial regulations and global standards developed by IMO. IMO regulations cover all kinds of technical matters pertaining to the safety of transportation and the prevention as well as the control of environment pollution from ships.

The requirements governing safe carriage of solid bulk cargoes are included in International Maritime Solid Bulk Cargoes Code (IMSBC Code) [IMO 2014]. IMSBC Code specifies requirements related to the safe regulations that cover:

- precautions before accepting cargoes for shipping,
- procedures for safe loading and carriage,
- primary hazards associated with the different types of solid bulk cargoes.

2. SOLID BULK CARGOES GROUP A

A vast amount of dry seaborne cargoes is carried in bulk form without any packaging. Generally, such cargoes consist of one homogeneous grade. The solid bulk cargoes categories are in three groups:

- A cargoes which may liquefy,
- B cargoes which possess a chemical hazard,
- C cargoes which are neither liable to liquefy nor possess chemical hazards.

Group A includes: metal ore concentrates, iron ore fines, coal (bitumins, antracite), fluorspar, nickel ore, and other fine-grained materials.

It is estimated that 2 bln of tonnes of metal ore concentrates are transported by sea every year. The safe transport of metal ore concentrates is a responsible task. Such materials have individual properties, special carriage requirements and associated difficulties. Before loading, it is essential to obtain current valid information from the shipper on the physical and chemical properties of the cargo presented by shipment.

Many mineral ore concentrates which are essentially insoluble in water and which contain mainly finely divided material, may liquefy during sea transportation if they contain an excessive amount of water when loaded or if they subsequently become wetted. In the case of wet concentrates, the material consists of mineral grains of the ore separated from crushed rock by flotation process, and containing water which may lead to liquefaction due to moisture migration.

Moisture migration is caused when vibration due to a ships engine or due to motion in heavy seas causes the water content of a cargo to rise to the bottom of the hold, which might eventually lead to a dangerous area. The cargo may shift dangerously from side to side. The presence of water on the surface of the cargo is also indicative of liquefaction

The basic idea of the requirement for the material which may liquefy is limitation of the moisture content of the cargo. It is vital that the moisture content of concentrates be analysed and checked prior to shipment, refused if this analysis reveals that the moisture content of the concentrates is too high.

Flow Moisture Point is moisture content, which allows for passing the bulk cargoes from solid into liquid state. To minimize the risk of liquefaction the IMSBC Code introduces the upper bound of moisture content of cargo, which is defined by the Transportable Moisture Limit (TML). TML represents the maximum moisture content of that cargo considered safe for carriage in ships.

To reduce and control the risk of liquefaction the shipper must supply to the master certificate stating the Transportable Moisture Limit (TML) and their actual moisture content. The actual moisture content of the cargo must be below the TML.

The current IMSBC Code specifies a schedule for the sea transportation of mineral concentrates classified as Group A and schedule for metal sulphide

concentrates as a Group A and B. These schedules are applied for a large number metal ore concentrates. Furthermore, the Code provides a number of schedules for individual concentrates (lead, manganese concentrates).

3. PROPERTIES OF METAL ORE CONCENTRATES

Ores and ore concentrates (products of mining) are solid materials that are often transported by sea, usually in bulk.

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 the 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. 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 friction coefficient.

When pressure of water in void becomes 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 [Youd 2003; Sieder and van den Beukel 2004]. Such phenomenon is called "liquefaction".

Density, moisture content, grain size distribution, permeability, bulk density are elementary ore concentrates properties which characterize the state of these cargoes.

Some of these soil properties can be used to estimate and control other types of properties such as shear strength, void ratio, the degree of humidity.

The moisture content is the crucial characteristics indicating the ability to liquefaction of fine-grained materials in the conditions of maritime transport. Liquefaction is unlikely to occur providing that when loaded it complies with the IMO requirement according to which the moisture content of the cargo is relatively uniform and below the TML.

Ore concentrates consist of particles of various shapes, sizes and quantity. The grain size analysis divides these particles into size groups and determines relative proportions by weight. Grain size analysis is a basic test that assesses whether the ore concentrate is able to liquefaction The liquefaction may take place when the content of grains with the size 0,3 mm and less is greater than 10% [Eckersley 1997].

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 [Bardet 1997].

According to the classification of soils, based on their coefficient of permeability, mineral concentrates are the materials with the low and medium degree of permeability [Head 1987]. 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. It is recognised that finer materials will liquefy more easily than coarser grained materials. In addition materials with a wide size distribution will tend to flow more easily and be more dangerous [Popek 2002].

In this paper there are presented the results of testing the three types of flotation concentrates taking into account the properties which significantly influence their safe shipment. The properties of these cargoes are discussed from the point of view of their safe shipment.

4. EXPERIMENTAL PROCEDURE

4.1. Materials

Used in the study metal ore concentrates are characterized by different origin, chemical composition and grinding:

- flotation lead concentrate: flotation galena,
- flotation copper concentrate,
- flotation zinc concentrate : zinc blende.

Flotation lead concentrate is composed mainly of PbS. The concentrate is produced in Ore Mining and Smelting Works in Bukowno. The water content in flotation lead concentrate is about 3,5–5%.

Zinc copper flotation, composed mainly of CuS, comes from the "Polkowice" Mining Works in ZGH Polska Miedź. The moisture content received in the sample was 5,4%.

Zinc blende flotation, composed mainly of ZnS, comes from the "Trzebionka" Mining Works in Trzebinia. The moisture content received in the sample was 5,4%. Flotation concentrates are produced in a flotation process with the use of flotation and foam generating chemicals.

All tested concentrates are typical materials, "which may liquefy". According to the classification of granular materials, regarding water permeability tested concentrates are classified as materials of medium permeability [Head 1987].

4.2. Methods

The ability for safe shipment by sea of ore concentrates was assessed on the basis of determination of the following parameters: grain size content, TML, permeability.

The samples have been tested in original state as delivered. The specific gravity of solid part of each sample has been measured using pycnometer.

The sieve analysis has been performed and effective D_{10} has been determined.

The Code of Safe Practice for Solid Bulk Cargoes recommends following methods for estimation FMP and TML :

- Flow Table Method,
- Japanese Penetration Method,
- ProctorC/Fagerberg Method.

The Flow Table is applicable to materials with a maximum size of 1 mm. It may be suitable for mineral concentrates with a maximum grain size up to 7 mm. The Penetration test is generally suitable for concentrates and coals up to a top size of 25 mm. The Proctor/Fagerberg Test may be used for both fine and relatively coarse-grained ore concentrates and similar materials up to a top size of 5 mm [IMO 2014].

The TML and FMP values of tested concentrates have been determined to use the three method recommended by IMSBC Code.

Evaluating the potential for liquefaction mineral concentrates was based on permeability changes of tested materials. Permeability of each sample was measured for reference, based on Polish Standards PN -55/B 04492 Estimation of the permeability coefficient.

In the experiments (estimation of the permeability) 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, $1,532 \times 10^4$ N/m², $3,0645 \times 10^4$ N/m², $4,589 \times 10^4$ N/m², $7,659 \times 10^4$ N/m² respectively. The test without any stress corresponds to the stress in the hold during the loading. Increasing values of normal stresses represent the changes in the bulk cargoes during the sea transportation.

4.3. Results

The results of estimation of specific gravity and bulk density of tested concentrates are shown in Table 1. The values are necessary for determining the TML values by means of the Proctor C/Fagerberg and Flow Table method.

Table 1. Specific gravity and bulk density of tested concentratesTabela 1. Wartość gęstości i gęstości objętościowej badanych koncentratów

Samples	Specific gravity [kG/dm³]	Bulk density [kG/dm³]	
Flotation galena	6,34	3,32	
Flotation copper concentrate	3,10	1,15	
Zinc blende	4,10	1,82	

Source: own study.

Grain size distribution have been measured for three tested samples. The results of the measurement are shown in Figure 1 in the form of the grain size distribution curves.



Fig. 1. The grain size distribution of tested materials

Rys. 1. Krzywe analizy ziarnowej badanych materiałów

Source: own study.

Between the tested concentrates there are differences in the particle size distribution due to different grinding processes of the rock materials. In the flotation lead concentrate the content of particles with a diameter smaller than 0,3 mm is essentially greater than 10% and amount 67%. The content of particles greater than 1 mm is about 17%.

In zinc blende concentrate the amount of particles smaller than 0,3 mm is increased to 75% and content of particles greater than 1mm does not exceed 13%. Deepening of the grinding process of the copper concentrate is demonstrated by increasing content of smaller grains. In this concentrate the content of the grains smaller than 0,3 mm is 85% and that of grains greater than 1 mm only 3%.

The grain size content of tested concentrates qualifies them as susceptible to liquefaction.

Changes in water permeability of mineral concentrates expressed as the permeability coefficient are presented in Table 2.

Normal stress [·10 ⁻⁴ N/m²]	Permeability coefficient k [m/s]			
	flotation galena	flotation copper concentrate	zinc blende	
0	8,00·10 ⁻³	2,00.10-4	8,00 [.] 10 ⁻⁵	
1,53	1,05·10 ⁻⁴	0,50·10 ⁻⁴	4,30 [.] 10 ⁻⁵	
3,06	1,20.10-4	1,30·10 ⁻⁵	1,20· 10 ⁻⁵	
4,60	8,02·10 ⁻⁵	0,90·10 ⁻⁵	6,80 [.] 10 ⁻⁶	
7,65	7,75·10⁻⁵	3,70·10 ⁻⁶	2,45·10 ⁻⁶	

Table 2.	Results	of	permeability	tests
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Tabela 2. Zmiany współczynników filtracji badanych koncentratów

Source: own study.

The nature and magnitude of compaction in fine-grained materials such as mineral concentrates significantly influences their mechanical behaviour. 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 concentrates without compaction corresponding to the loosely cargo, shortly after loading. The largest value of permeability coefficient is observed for flotation galena, which consists of relatively large mineral particles, in comparison with copper and zinc concentrates. Flotation copper concentrate and zinc blende have similar particle size distribution. Different to the alignment of mineral particles causes the copper concentrate has a greater porosity ratio than zinc blende; in consequence the filtration coefficient of copper concentrate is significantly greater than coefficient of zinc blende.

Compaction modifies the permeability by decreasing the voids available for flow, and reorienting particles. In consequence the reduction of the ability to filtration is observed.

The results of estimation of TML in tested concentrates are presented in Table 3.

 $\label{eq:table 3. TML values determined by means of method recommended by IMSBC \ Code$

Samples	TML [%]			
Samples	Proctor/Fagerberg	Flow Table	Penetration Test	
Flotation galena	7,80	6,50	6,70	
Flotation copper concentrate	13,74	11,50	11,90	
Zinc blende	10,90	9,30	8,90	

Tabela 3. Wartości TML wyznaczane metodami zalecanymi w Kodeksie IMSBC

Source: own study.

The value of transportable moisture limit of the fine-grained concentrates is tightly related to the grain size distribution.

The results of estimation of TML obtained using Proctor C/Fagerberg Method are higher in all cases than those given by remaining used methods. The results of FMP determination obtained using Penetration Method are consistent with those got from the Flow Table Method.

Taking into consideration the fact that the safe shipment of bulk cargoes is very important, the Penetration Method and Flow Table Method should be recommended for determination of Transportable Moisture Limit.

5. CONCLUSION

The sea transportation of solid bulk cargoes is controlled through various international regulations, each aiming to prevent or reduce the impact on a man, environment and property during transport.

In this paper the properties of different flotation concentrates are presented and are discussed from the point of view of their safe shipment. These concentrates should be tested in order to determine their TML values and will be accepted for shipping by sea if their current moisture content is lower than their TML values.

The liquefaction phenomenon is deeply related to the characteristics of drainage of the water and grain size distribution.

Permeability is an important parameter, determining the ability to liquefy the solid bulk cargoes in conditions of maritime transport. Liquefaction becomes first at the bottom layer of cargo as a result of filtration of water from the upper layers of cargo and therefore permeability values should be determined.

Basing on the results of the tests, the effect of different compaction of the samples on the permeability was observed. The maximum value of permeability coefficient was achieved for concentrate without any stress.

The increasing values of normal stresses tend to the reduction the degree of permeability.

The course of grain size distribution curves indicates that all tested concentrates are susceptible to liquefaction in sea voyage as in each case the content of grains smaller than 0,3 mm is greater than 10%.

The comparison of the TML values confirms that the correlation occurs between the grain content and TML value. The transportable moisture limit increases along with the concentrate disintegration increasing.

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