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The Influence of Organic Polymer on Parameters Determining Ability to Liquefaction of Mineral Concentrates

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ABSTRACT: When the wet granular materials lose their shear strength they flow like fluids. This phenomenon is called liquefaction. The liquefaction can be prevented by means of limiting the moisture content of cargo by introducing the safety margin. Cargoes, which may liquefy shall only be accepted for loading when the actual moisture content of the cargo is less than its Transportable Moisture Limit (TML). It has been recognized that in some cargoes, moisture can gravity drain towards the bottom of the hold. The resulting much wetter bottom layer may therefore be prone to liquefaction and provoke instability of the entire cargo.
To prevent sliding and shifting of ore concentrates in storage a biodegradable materials are added to the ore. The polymer materials absorb water from the ore particle's pores and the moisture content goes down. In consequence polymer materials may prevent drainage of the water from the ore particle's pore.

1 INTRODUCTION

Bulk shipping has been used for many years to reduce the cost of sea transport and the transport of bulk cargoes is a vital component of international trade. Such trades 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 (Roberts M. & Marlow P. 2004).

In recent years, bulk carriers have been identified with the high risk of catastrophic structural failure and foundering, and with heavy loss of human life. Several risk factors have been identified that had significant, independent effect upon the likelihood of a bulk carrier foundering. Ore concentrates and other similar fine-grained materials transported by sea belong to hazardous materials when are considered as bulk cargoes (materials MHB). This type of cargoes is transported in a wet state.

Excessively wet cargo can pass into liquid state in sea transport conditions (Zhan M. 2005, Shitharam T. G. 2003). According to the Code of Safe Practice for Solid Bulk Cargoes (BC Code) (International Maritime Organization 2004), deterioration or loss of ship's stability is one of three basic hazards, which are bound with sea shipment of ore concentrates and other fine-grained cargoes. Too high humidity of cargo leading to its liquefaction may cause shift of the cargo and in consequence ship's heel and even its capsizing and sinking.

The International Maritime Organization (IMO), recognising that some losses had occurred due to improper loading, issued a code of practice for these operations. The probability of a hazard developing into an undesirable consequence is focus of safety management and safety regulation. The recent publication of recommendation guidelines for cargo–handling operations and the amendments to the International Convention for the Safety of Life at Sea contribute to the decrease the possibility of occurrence the liquefaction during sea transportation (International Chamber of Shipping1999, BLU Code London, (2004)).

To better illustrate liquefaction mechanism three-phase structure of ore concentrates and similar materials is considered, which consist of solids (mineral grains), water and air.

Mineral grains are very small; they are from 0,001mm to several millimeters 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. The inter-grain pores are contracted in sea transport conditions due to ship rolling and vibration. The air, permeability coefficient of which is about 500 times greater than that of water, first escapes, thus full water saturation of pores is affected.

Full compressive stress is thus applied to the incompressible water in the pores between mineral grains which causes drop of inter-grain friction, i.e. ore liquefaction and in consequence possible shift of cargo (Michałowski & others 1995).

The possibility of instability because of liquefaction of bulk cargoes such as mineral concentrates has been recognized for some time. BC Code includes several provisions aimed to prevent the movement of bulk cargoes either by sliding or liquefaction

Moisture content allowing to passing of a bulk cargo from solid into liquid state is called critical moisture content. One of its possible measures is Flow Moisture Point (FMP). On its basis permissible moisture limits for shipment conditions are determined. Transportable Moisture Limit (TML) is such moisture content at or below which a loose cargo can be transported in bulk on ships without danger of passing of the cargo into liquid state. Its usually calculated as 90% of FMP. The possibility of instability because of liquefaction of bulk cargoes such as mineral concentrates has been recognized for some time. Many cases are reported of large heel of a ship or even her sinking due to cargo liquefaction. A cargo, which is liable to liquefaction, must be sufficiently fine grained (so that permeability is sufficiently low) and have a high enough initial moisture content:

For cargoes with permeability so low that virtually no moisture redistribution occurs during voyage, the initial moisture content needs to be below the transportable moisture limit so that the whole cargo does not liquefy as a result of the ship's motion during heavy weather.

For cargoes that are relatively free draining, redistribution occurs with moisture from the upper levels of the cargo draining towards the base. Unless efficiently drained the bilges, this water saturates the bottom levels of the cargo and liquefaction could occur with cargo shifting during heavy rolling motions (Eckerley J.D. 1997).

These cargoes, prone to liquefaction, should never be carried without checking the moisture content. The Code of Safe Practice for Solid Bulk Cargoes 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 transportable moisture limit. The cargoes which may liquefy shall only be accepted for loading when the actual moisture content of the cargo is less then its Transportable Moisture Content and refused if the analysis reveals that it's moisture content is too high. The Code provides information how the moisture content of ores concentrates can be tested and assessed.

For liquefaction the cargo needs to have permeability low enough that excess pore pressures cannot dissipate before sliding occurs. This condition is controlled by the material's grain size distribution, and Kirby expressed this in requirement that 95 percent or more of the cargo should be coarser than 1mm to prevent liquefaction. In soil mechanics literature the requirement is usually expressed as $0{,}006\text{mm} < d10 < 0{,}3$ mm for liquefaction to be likely, where d10 represents the particle size for which only ten percent by mass of the material is finer (Eckerley J.D. 1987).

A large group of organic polymers fined use in the mineral industry with the specific function [Bulatovic 1997]. 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. Starch can be found in plants as a mixture of two polysaccharides: amylase, the nearly linear polymer consisting of α – (1, 4)-anhydroglucose units, and amylopectin, a group which is able to undergo substitution reactions and C-O-C linkage responsible for the molecular chain braking. The OH group has a nucleophilic character and by reaction with different reagents it is possible to obtain a series of compounds of modified properties. Chemical and physical properties of starch have been widely investigated due to its easy to be converted into a thermoplastic and then be used in different applications (Tudorachi N. & others 2006). Starch based blends present enormous potential to be widely used in environmental fields, as they are totally biodegradable, inexpensive (when compared to other biodegradable polymers). The material containing starch gets destroyed when exposed to environmental factors, since due to starch hydrolysis its structure becomes weaker, and after some time, under certain conditions, synthetic polymers contained in the product also undergo decomposition.

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. The properties and the processing procedures of biodegradable starch – based thermoplastic blends, like starch/polycaprolactone, starch/cellulose have been already reported (Demirgoz & others, 2000).

2 EXPERIMENTAL PROCEDURES

2.1 *Material*

The iron concentrate was used for the tests.

It is a product of a gravimetric separation of large mineral particles. The iron concentrate is a fine material which is empirically judged as "which may liquefy if shipped above the TML".

Following polymer materials were tested: polymer material Y (made of thermoplastic starch and cellulose derivatives from natural origin) and polymer material Z (made of starch and policaprolactone).

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

Based on the results of estimation the ability to absorb of water by polymers materials it can be said that polymer material Y absorbs more water then polymer material Z. The equilibrium absorption of polymer Y is reached in 48 hours. The time taken to reach equilibrium water content in polymer Z is shorter – about 18 hours.

Water uptake is affected by the type of polymer. The time required to reach equilibrium water uptake is lower for blend containing starch and polycaprolactone then for blend containing starch and cellulose (Popek M. 2005).

The samples of polymer materials were in granular form. The experiments were conducted for samples of concentrate: without polymer materials and for mixtures contain 98 % concentrate and 2 % of polymer materials.

The course of grain size distribution curves indicates that all the tested samples are susceptible to liquefaction in sea transportation conditions as in each case the content of grains smaller then 0,3mm is greater then 10 %. The content percentage values of the grains (of the size below 0,3mm) in concentrate without polymer is 76,9 %. In mixtures of concentrate and polymer materials the contents of particles with a diameter smaller than 0,3mm are negligible smaller and amount 76,0 % for mixture with polymer Y and 76,1 % for mixture with polymer Z. the results of grain size analysis indicate that polymers do not significantly change grain size distribution. This is the reason why all tested samples may liquefy.

2.2 *Methods*

Following tests have been carried out:

- Estimation of TML:
  The International Maritime Organization approved, in the Code of Safe Practice for Solid Bulk Cargoes the following assessment methods of safe moisture content in the cargoes: Flow Table Method, Japanese Penetration Method and proctor/ Fagerberg Method. The evaluation of FMP was performed with the use of the Proctor Fagerberg Test. Proctor/ Fagerberg Method is recommended for evaluation of some fine-grained bulk cargoes. The sample was consolidated by 25 drops of rammer from 0,2 m height in the measuring cylinder, layer by layer, repeating the procedure 5 times and finally weighing the cylinder with the moist sample. Then volumetric density of the wet concentrate γ_{0b} and of the dry consolidated concentrate γ_{0bjs} were calculated and a consolidation curve γ_{0bjs} – f(w) drawn, where "w" stands for moisture content percentage in relation either to wet concentrate weight. TML was determined from a cross point of the void ratio curve and a line of 70 % degree of saturation, theoretically calculated.
- Permeability of concentrates:
  The permeability is the rate at which water under pressure can diffuse through the voids in the mineral concentrates. These materials 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 and internal friction angle:
  The estimation of cohesion and internal friction angle were 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 (estimation of the permeability and the cohesion and internal friction angle) 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 *104 N/m2, 3, 0645 *104 N/m2, 4,589 *104 N/m2, 7,659 *104 N/m2 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 DISCUSSION

3.1 *Estimation of TML*

The results obtained by using Proctor/ Fagerberg test are shown in Figures 1-2. The figures show Void Ratio as a function of net moisture content by volume. In each figure, the ordinate and abscissa denote void ratio and net moisture content by volume, respectively. The black circles indicate the measured data. The straight line corresponds to degree of saturation 70 % theoretically calculated. TML was determined from a cross point of the experimental curve and a line of 70 % degree of saturation.

The obtained results are presented in Table 1.

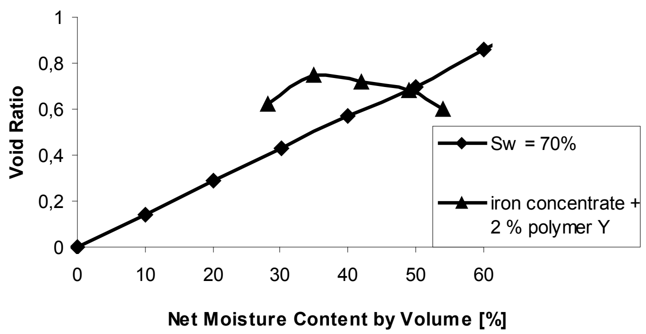

Figure 1. Compaction curve for iron concentrate + 2% polymer Y.

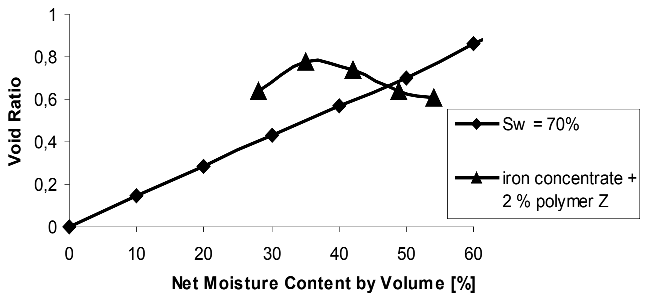

Figure 2. Compaction curve for iron concentrate + 2% polymer Z.

Table1. Transportable Moisture Limit determined by Proctor Fagerberg test

Sample	Specific gravity of solid	Transportable Limit of Net Moisture Content by Volume	TML
Iron concentrate + 2 % polymer Y	4,98	49 %	9,02
Iron concentrate + 2 % polymer Z	4,98	47,5 %	8,7

Despite the presence of polymer in tested concentrate, the values of estimated TML are similar, because liquefaction is tightly related to the grain size contents.

3.2 *Permeability*

The results of permeability test are presented in Table 2.

Table 2. Results of permeability test

Normal stress [N/m^2]	permeability coefficient k [m/s]	
	Iron concentrate + 2 % polymer Y	Iron concentrate + 2 % polymer Z
0	14,0*10^{-3}	15,2*10^{-3}
1,532* 10^4	8,5*10^{-3}	9,2*10^{-3}
3,064* 10^4	7,1*10^{-3}	8,8*10^{-3}
4,589* 10^4	5,2*10^{-3}	7,5*10^{-3}
7,659* 10^4	3,5*10^{-3}	5,15*10^{-3}

The compaction modifies permeability of samples by decreasing the voids available for flow and reorienting particles. Based on the results the effect of different compaction of the samples on the permeability was observed. The maximum values of permeability coefficient k were achieved for samples without any stress. The increase of consolidation force caused decreases the value of the permeability coefficient. The ability to permeability of mixtures is related to the composition of the polymer material. In all cases, for samples with polymer material Y, the higher decrease of permeability was obtained.

3.3 *Cohesion and internal friction angle*

The changes of internal friction angle as a function of moisture content are presented in Figures 3-4.

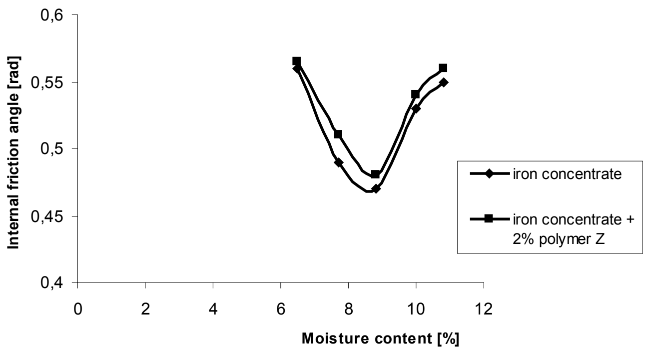

Fig.3 Internal friction angle for iron concentrate + 2% polymer Y.

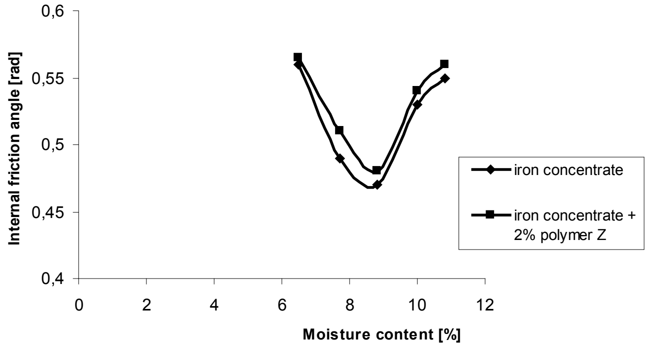

Figure 4. Internal friction angle for iron concentrate + 2% polymer Z.

As a result of performed test it can be said that internal friction angle reaches minimum value when moisture content is chosen to TML. The presence of polymer material in tested sample influences on the value of internal friction angle. In each case the values are higher than those for sample without polymer material.

The cohesion as a function of moisture content are presented in Figures 5-6.

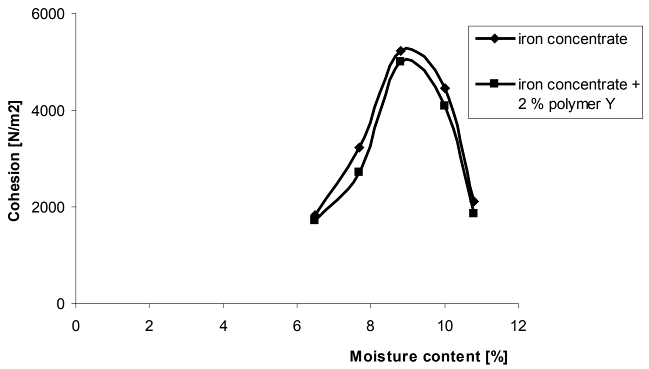

Figure 5. Cohesion for iron concentrate + 2% polymer Y

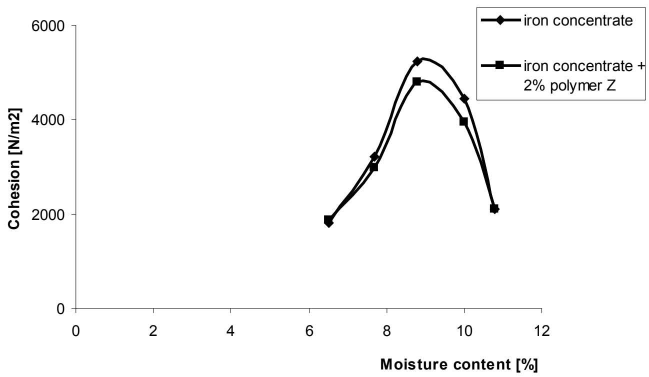

Figure 6. Cohesion for iron concentrate + 2 % polymer Z.

The apparent cohesion does not occur in dry materials with pores entirely filled with air nor in moist materials having pores entirely filled with water. In all samples cohesion increases with the increasing content of water and it reaches a maximum value with moisture approaching the TML and then it goes down. The presence of polymer material in tested sample significantly changes values of cohesion. Decreasing values of cohesion, for each moisture content, is observed.

4 CONCLUSIONS

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

The comparison of the TML values confirms that the correlation between the grain content and TML values occurs.

The presence of polymer material in tested sample influences on the values of cohesion and internal friction angle but the extreme values are reached at the same moisture content.

The nature and magnitude of compaction in fine – grained materials such as mineral concentrates significantly influences their mechanical behavior. Increasing values of normal stresses tends to reduction the degree of permeability.

In consequence, 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, before the transportation by sea. These materials are particularly attractive because they are based on natural renewable resources, which are environmentally friendly.

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