

Comparative study on the un test n`5 application on cargoes that emit flammable gases similar to dri c that requires ventilation

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Abstract: This technical note summarizes a technical comparison of common testing procedures, as well as reviewed of the UN Test N` 5, for the assessment of the self-heating properties of cargoes and materials that has shown a clear trend on maritime fire and explosions events, as well as considering of external factors that can combine self-heating and emit flammable gases to conclude in an unlikely event affecting the security of crews and ships. A high understanding of the external factors effect on the cargo materials certainly will help the application of spontaneous reactions management actions (SRMA) on board of ships during the cargo sea passage. The intended comparison is based on laboratory, industry and field observations and data, whereas the among the external factors considered are, moisture content, stockpile procedure and aging, air velocities and moderate pressures internal and externally to the cargo material. The comparison results have shown that the self-heating and the flammable gas emissions has a common pattern when reacting with any oxygen available source, regardless the reactive material chemical composition.

Keywords: Reactive materials, self-heating, self-ignition, Direct reduced iron fines, materials handling, UN test N` 5, maritime safety, spontaneous reactions, risk management. IMSBC Code , IMO

Estudio comparativo de la aplicación de un test n`5 en cargas que emiten gases inflamables similares a dri c que requieren ventilación

Resumen: Estas notas técnicas resumen una comparación técnica de los procedimientos de ensayos comúnmente aceptados, así como una revisión del ensayo UN Test N` 5, para la cuantificación de la tendencia de las propiedades de loa materiales de cargas marítimas riesgosas que puedan causar eventos de incendios y explosiones en buques durante su transporte, considerando además de aquellos factores externos a la carga que cuando se combinan producen auto calentamiento y generación de gases inflamables que conllevan a eventos que afectan tanto la seguridad de las tripulaciones y a los buques de transporte. Por tanto, un elevado nivel de comprensión de los efectos que factores externos involucrados ciertamente ayudara a la aplicación y ejecución de un plan y acciones para el manejo de las reacciones espontaneas (AMRE) a bordo de los buques durante la travesía de dichas cargas, lo cual requiere un nuevo enfoque para las consideraciones de los efectos de dichos factores externos identificados sobre los materiales riesgosos y el umbral para su propensión para autocalentamiento e ignición. La comparación intentada se basa en el análisis de datos disponibles tanto de laboratorio como de observaciones y mediciones de campo en buques y en sitios de almacenamiento, mientras que entre los factores externos se han considerado la humedad de los materiales, procedimientos de almacenamiento, envejecimiento, velocidad de aire alrededor de los materiales, nivel de presiones moderadas tanto internas como externas al material y los métodos de manejo de materiales. Los resultados de la comparación demuestran que los fenómenos de autocalentamiento y de emisión de gases tienen un patrón común cuando los materiales reaccionan con cualquier fuente de oxígeno, independientemente de la composición química de los materiales que reaccionan

Palabras Clave: Materiales reactivos, auto calentamiento, auto ignición, Hierro de reducción directa, manejo de materiales, UN test N` 5, seguridad marítima, combustión espontánea, gerencia de riesgos, Código IMSBC. OMI

I. INTRODUCTION

The ventilation requirements as described in the IMO IMSBC Code are briefly described in Section 3.4.2 clearly specifies that cargoes that may emit flammable gases in sufficient quantities to constitute a fire or explosion hazard should be effectively ventilated as necessary. In Section 3.5.1 of the IMSBC Code also specifies that when cargoes which may emit flammable gases are carried, the cargo spaces shall be provided with mechanical ventilation. Example of cargoes containing metals that emit flammable gases after in contact with water listed in the IMSBC Code are: Aluminum Ferrosilicon Powder forms, Aluminum Smelting By-products or Aluminum Remelting By-products UN 3170, Ferro phosphorus (including briquettes), Ferrosilicon UN 1408, Magnesium powders, Silicon-manganese (low carbon), Zinc Ashes UN 1435, Direct Reduced Iron Fines, pellets and lumps.

These cargoes that require ventilation are listed among others of nonmetallic content such as grains, coal, seed cake etc. In this report are compared the trends of the temperature ($^{\circ}\text{C}$) increase and the hydrogen gas emissions expressed in $\text{lt}/\text{kg}\cdot\text{h}$, regardless the type of the glassware test rig used till present but also includes electric grounding of metallic containers and cathodic protection systems on ships. ajo.

II. PROPENSITY OF CARGOES TO SELF-HEATING

The basic reactions for heat generation is the oxidation of the material surface reacting with either air or any other oxygen supply source, which leads in the need for a new approach considering the combined effect of external factors such as air low velocities, impressed DC currents, variable moisture content during stockpiling, moderated low pressure.

Low air velocities and low pressure around the cargoes particles affects the dissipation of newly formed gases reaching the cargo surfaces, such as in the coals gases methane, hydrogen sulphide, carbon monoxide and hydrogen, the two former gases are also common in the case of DRI's, as per the material considered thus depriving the oxygen availability at the particle surfaces whereas high differential pressure will remove the oxidation gases away from the particle surfaces, in either cases the fire risks is less likely to occur. Finally, the threshold point when the required adequate pressure and air flow are appropriate for the self-ignition to occur must be avoided.

A. The stockpiling self-heating mechanism

The self-heating and ignition of coal in stockpiles has been fully studied as show in Fig. 1, from this figure several internal reactive layers are identified in which the heat is different and under such conditions different gas emissions and oxidation reactions occurs, to finally due to its high reactivity enough heat is evolved to ignite the coal.

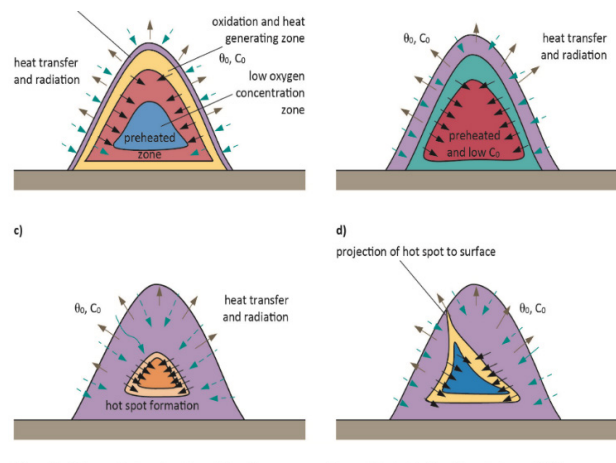


Fig. 1.- Stockpile steps followed for evolving heat and further ignition of coal [2]

A similar mechanism is followed by DRI C Fines stockpiles as show in Fig. 2, showing the temperature measures in a stockpiling yard at the open sky.

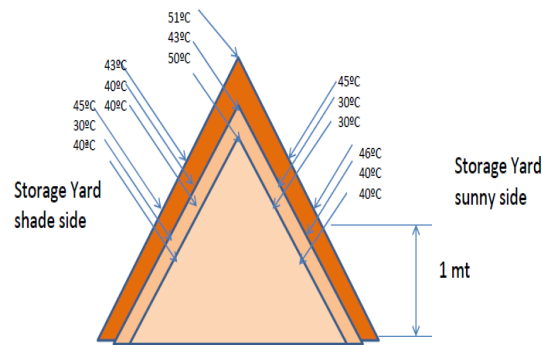


Fig. 2.-Open sky field temperature readings on a DRI C Fines stockpile [15]

In the inner zone of the pile there is an oxygen depletion due to the high bulk density of the of about 3300 kg/m³, the associated low porosity only allows the oxygen source from the moisture content. The heat evolved by the oxidation reactions increases the temperature up to near the 100 degrees centigrade, according to the mechanism show in Fig. 3 [8].

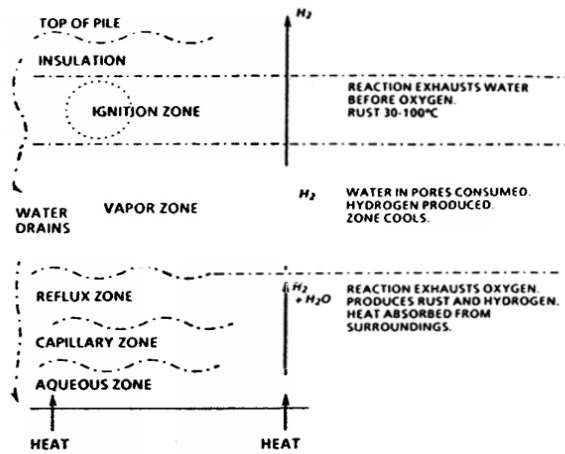


Fig. 3.- DRI C iron rust formation stage [8]

B.The materials handling.

In regard of the assessment of the material handling method effect on the DRI C temperature evolution to take care of the maximum allowed loading temperature, a field measurements program was set. The program did include the conveyor belts length, speed and the material dropping height from the ship loader to the ship holds bottom floor, results are presented in Tabl 1.

Table 1. DRI C Fines temperature in ship holds as a function of material temperature in stockpile yard

Time min	Loading Temp (°C)			
	40 °C	48 °C	55 °C	65 °C
1	42,95	50,95	57,95	67,95
4	45,9	52,58	59,58	69,58
18	47,53	48,05	55,05	65,05
22	43	41,76	48,76	58,76
24	36,71	34,59	41,59	51,59
35	81,6	79,48	86,48	96,48

The effect of the materials handling on the temperature increase of the material in the ship holds, could be related with the exposure of fresh reactive surfaces by possible breakage of lumps in for instance coal and DRI in either forms of pellets or briquettes. This effect is schematically show in Fig. 4.

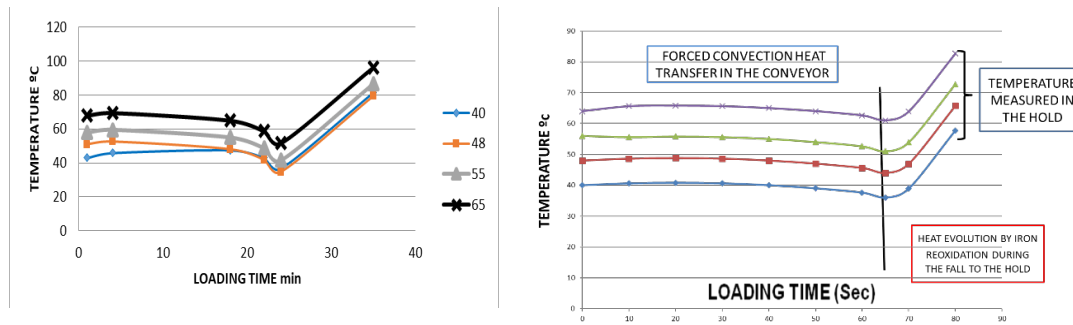


Fig. 4.- Temperature profile of DRI Fines from stockpile to ship hold (Left), Temperature profile of loading DRI Fines at the hold (right)

The shown temperature trend can be related to the air flow over the material surface on the forced convection effect when being conveyed from the yard towards the ship unloading end, whereas the increase of the temperature levels is related to the fine particles reacting surface during the free falling through the air towards the holds bottom. The analysis of the obtained field observations is mathematically expressed by means of a polynomial equation obtained from a minimum square regression from the function in Fig. 5.

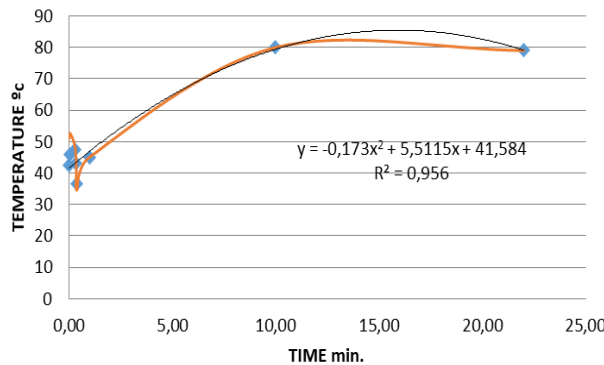


Fig. 5.-Temperature evolution of CRI C Fines during loading from stockpile yard

C.Loading Procedures

For the loading the hazardous materials in Chapter VII of the IMSBC Code it is clearly established loading temperature requirements, as show in Table 2.

Table 2. Suggested loading temperature of selected materials IMSBC Code

Material	Brown Coal	Coal	Pet Coke	DRI C	Seed cake
Loading Temp `C	< 30	< 55	< 70	< 107	< 55

As described earlier, the temperature increase, expressed in `C/min, of the materials is an important issue and its related to variables such as flash point, heat generation and flammable gasses emissions. The R70 test index is associated to coal reactivity described as low reactivity when is less than 99 `C/h and high reactivity is assumed to be less than 0.5 `C/h. In the particular case of coals, the threshold temperature is measures though the R70 adiabatic and non-isothermal heating tests, for the DRI C Fines the value was derived from actual field readings on board of ship cargoes. The results are show in Fig. 6, for low Sulphur, low ash subbituminous coal having high tendency for self-heating (coal A) and a less reactive bituminous coal, whereas in Fig. 7 is show a very low reactive and prone to self-heating of DR C Fines, when comate with coal.

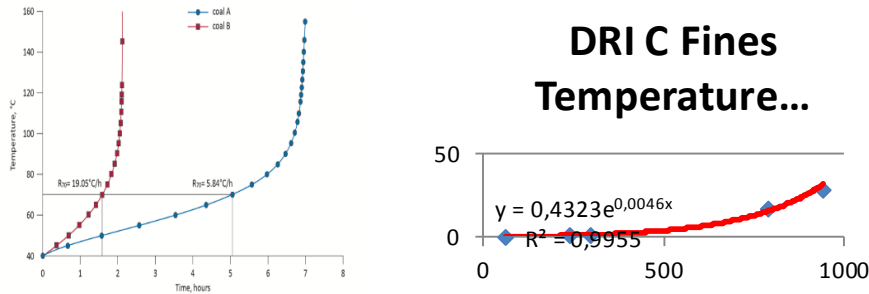


Fig. 6. - R70 values for different coals (left), coal B has higher R70 value meaning less reactive for heating up [2], thermal inertia of DRI C Fines.

Regarding the combined effect of the loading temperature and moisture content on the flammable gas generation in glassware reactor, is clearly show in Fig. 7 and 9.

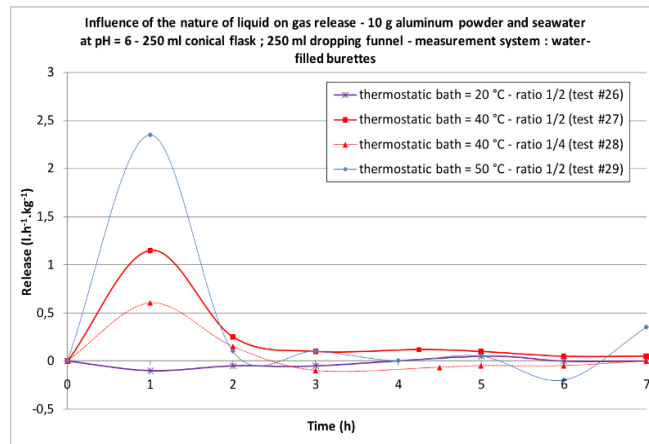


Fig. 7.- Influence of seawater on gas emissions from aluminum powder [3]

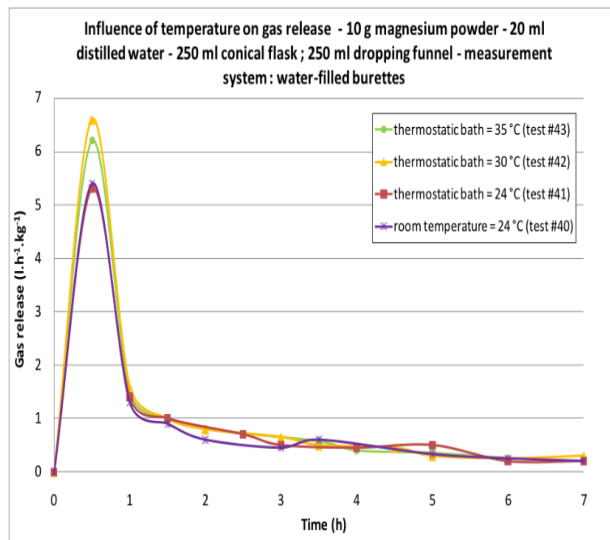


Fig. 8.- Influence of temperature on gas emissions from magnesium powder [3]

D.Moisture type and quality

The moisture content as well as the type it, acting on the material is another important variable for the intended purpose, but quality wise it turns to be close related to its electric conductivity and the corresponding effect via the pH values. This is a general application for the hazardous cargoes when considering the clear effect on temperature increase, heat generation and gas emissions rates especially when DC energy is present, which applies for the galvanic mechanism in batteries design and operation.

The temperature evolution measured in °C/min in the material is a function of the moisture content and it is considered a low rate when the temperature level remains steady and considered high when the rate in the temperature levels initially is high, followed by an steady period because of the moisture evaporation in the range of 80 to 90 °C, when full moisture evaporation is achieved a rapid temperature increase appears until it reaches a runaway overpassing the either the self-heating or ignition threshold for a fire/explosion event. This effect is show in Fig. 9.

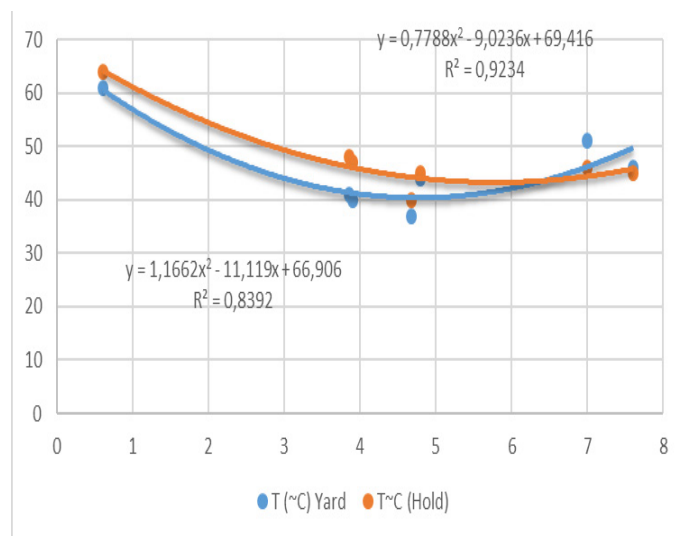


Fig. 9.- Effect of % moisture on DRI Fines temperature variation from yard to ship hold

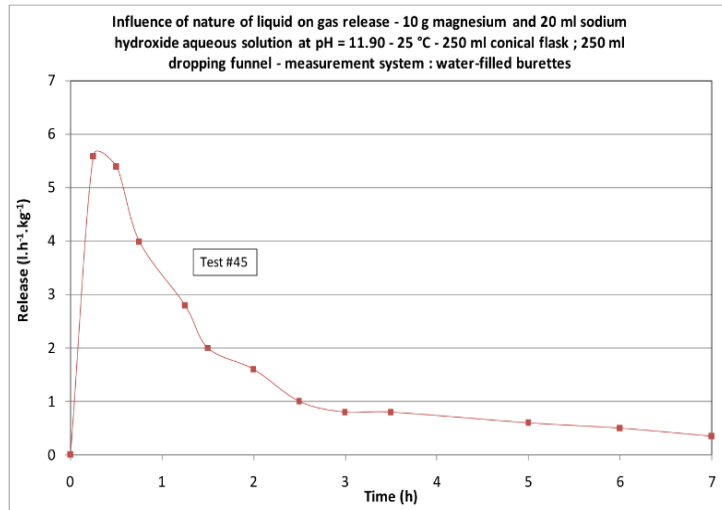


Fig. 10.- Influence of sodium hydroxide (pH 11) on gas emissions from aluminum powder [3]

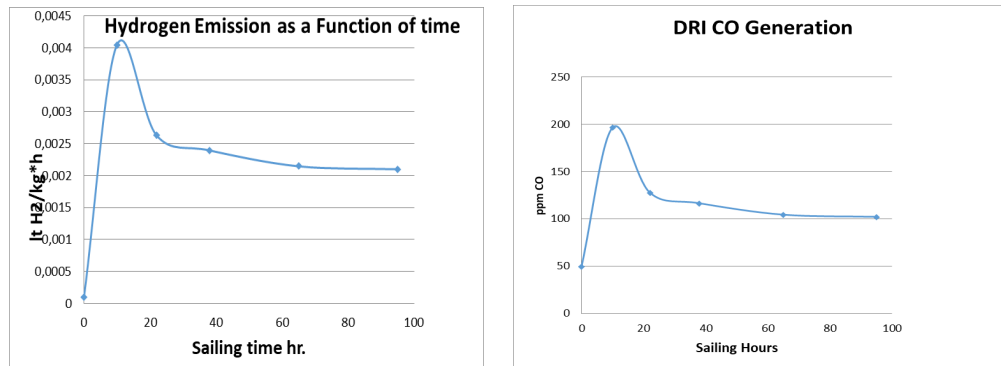


Fig. 11.- DRI C Hydrogen and carbon monoxide gas emissions during the ship sea passage under DC cathodic protection application.

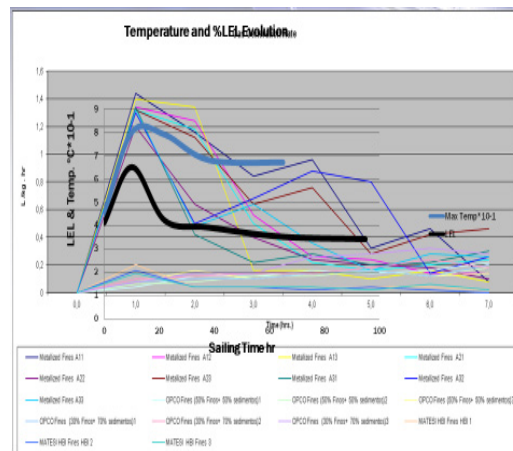


Fig. 12.- Hydrogen emissions and Lower Explosivity Level (LEL) of different DRI C Fines of moisture content between 3 and 7 weight percent (upper curves.)

It is worth noticing that the curves shapes in Fig. 7, 8,10, 11 and 12 shows the same pattern, which can be described by the following mathematical function

$$F. Y = k \times \exp b e \exp (-c x). \quad (1)$$

Where k, b and c constants values are particular for a particular material, this is expected to be so based on the different energies of activation (Ea), threshold temperature, and electric properties.

E. Direct Current (DC) energy source effect

Electric current can be conducted by and through any material either containing water or wet, including wood, therefore a reasonable approach to materials properties such as electric conductivity (S m) and resistivity (ohms mt) and establish its relation to the direct current (DC) energy supply by the cathodic protection systems (CP) used for corrosion prevention of any metallic container. Using this approach it is unavoidable not to consider Ohm's, Faraday laws as well as the Joule/thompson effect on the cathodic container/anodic cargoes. In the former portion of the system is unavoidable the hydrogen gas generation and heat release. Most of the hazardous cargoes listed in the IMSBC Code contains moisture, among which are grains, wood chips and logs, coal, DRI's, ferrosilicon and metal containing powders. In Table 3 are shown some conductivity and resistivity of selected materials.

Table 3. Resistivity and resistivity values of selected materials

Material	% H2O	Resistivity (Ω-m)
Coal	1-3	0.012-0.032* 10Exp 6
Coke	2.14-1.47	0.20 – 0.50
DRI A	1 max.	0.000588
DRI C	0 -12	0.0005888

When comparing gas emission from DRI C Fines applying the UN Test N` 5 laboratory conditions (glassware testing rig) with 200 kg sample in a steel container (grounded with CP) and a modified UN Test N` 5 using a DC energy source by Impressed Current Cathodic Protection (ICCP), the last two testing procedures show a substantial difference to those obtained in a glassware containers. Results are shown in Table 4.

Table 4. Effect of the test container on the results of UN Test N` 5

Test Conditions	Max. Hydrogen Rate lt./kg.hr.	% Variation	LEL Hold 3888 empty space m3
Inert Gas (IMO/UN) Glassware	0.00191	NA	1.61
Natural Surface Ventilation (Industry)	0.00195	0,5	1.63
Industry test steel container CP grounded	0.0040	161	3,34
Galvanic ICCP DC energy	0.0330	1680	4,48

Besides the DRI C Fines consideration as a reactive material under CP conditions, other iron containing materials such as ferrosilicon, it is worth considering its electric characteristics that turns this material as a highly reactive material to emit hydrogen gas. Very early on the XX Century, it was well known the use of fe-

ferrosilicon as a material to mix with sodium hydroxide before water was added for the hydrogen gas generation. The IMO received an event occurred to the MV AB Bilbao bulk carrier, IMO Number 9130200, reported during 2001, when sailing by the North Sea carrying 3000 metric tons of ferrosilicon. The cause of the accident was holds explosion by the accumulation of hydrogen gas. Although no further comments were found, there is a reasonable doubt that the cargo could be possible either contaminated with other sodium containing chemicals, or got in contact with sea water which also contains sodium and magnesium chlorides. Under those conditions, and the galvanic cell condition between ferrosilicon anodic cargo and the steel floor of the cargo hold, the only requirement to connect the galvanic cell was the presence of the electrolyte, this is the sea water. If this was the case, hydrogen gas was released and under natural ventilation hydrogen accumulation could be a cause for the explosion but even though a source of ignition was needed. In all cases involving DRI C fines and ferroalloys the oxygen depletion for whatever reason due to the accumulation of Hydrogen and carbon monoxide gas, under low air velocity, in either moderate or low pressure and oxygen depletion by actions of water steam and carbon monoxide emissions in the cargo open space environment.

III. MATERIALS REACTIVITY LEVEL AND ACCIDENTS OCCURRENCE

Aiming to obtain a clear relationship between the external factors and the material tendency to accidents and its intrinsic physical and chemical properties, the selected common property is the electric resistivity, in Fig. 13 is shown the assumed variable.

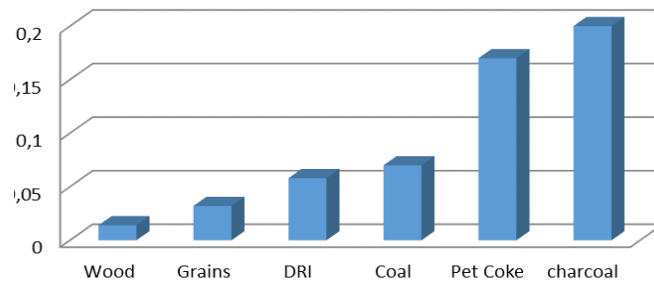


Fig. 13. Cargo materials electric resistivity (ohms cm)

As expected, the materials selected in Fig. 13 also have an specific energy of activation (E_a) expressed in kJ/mol, then the former variable indicates how easy the material could be for reacting under certain available heat generation, of course also depending on the moisture content, therefore it is possible to obtain an empirical and qualitative relationship with the fire and explosions frequency, as shown in Fig. 14.

Materials electric resistivity, Energy of activation (E_a) and Accidents frequency

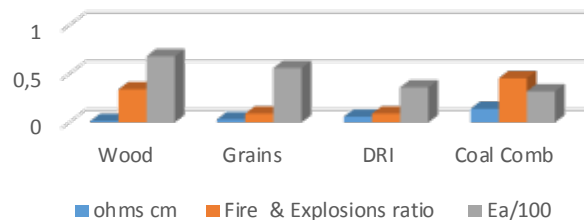


Fig. 14. Materials electric resistivity (ohms cm), energy of activation (E_a , kJ/mol) relationship with the fire and explosions accidents in ships.

Finally, the low fire and explosions index for DRI C Fines compared to coal cargo events can be explained based on the very low Ea value which turns to be a very low reactivity possible related to the moisture content as compared with the coal moisture content, as well as other type and amount and reactivity of the flammable gas emissions in the surrounding air (CH4 5-15.4%, H2S 4.5-4.5 %, CO 29% and H2 4%), this trend is show in Fig. 15.

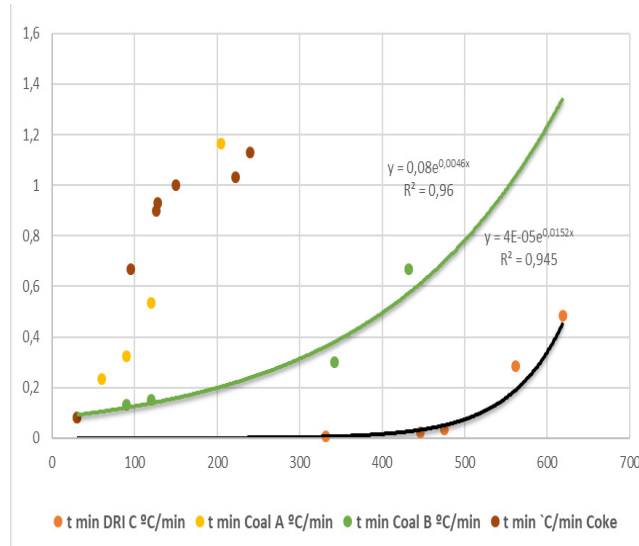


Fig. 16. Temperature variation rate (°C/min) comparison between DRI C Fines (1/100) and high and low reactivity coals and coke (left hand values).

IV.CONCLUSIONS

From the above comparative research, especially when considering the external factors influence on the self-heating and further ignition of the materials, it is possible to derive the following conclusions for further research work.

1.This research has proven the importance of considering the external factors on the reactivity of self-heating cargoes. Among these external factors the most important is considered to be the DC important is the direct current (DC) energy supplied by the cathodic protection systems in either ships or metallic containers. Consequently, the DC factor is recommended to be included in a reviewed and updated UN Test N` 5 for a more representative of the considered studied system and abstention of highly reliable results.

2.Reactive materials such as coal and DRI C Fines, when in stockpiled in yards are safe in open spaces in both extremes of the air circulation, this is in low and extreme air circulation. When the air circulation is low the accumulation of gases on the reactive surface tends to deplete the oxygen concentration reducing the reaction rate, whereas when high the removal of the flammable gases as well as the heat generated by the oxidation reactions

3.The compaction degree of the stockpile, in stockyards and ship holds, to reduce the presence of air is a concept to review to prevent ignition events rather than attempting to increase ventilation or inerting, the former leads to an accumulation of flammable gases.

4.The materials handling systems tends to increase new reactive surfaces when reclaiming fine materials such as DRI C and powders also increases the generation of fines and small particles in lumpy material such as coal.

5.It was found a close relationship between the moisture content in or around the materials, handling methods, energy of activation, liquid type and quality and the overall electric parameters considering the cathodic protection systems and the occurrence of fires and explosions in ship safety events

6.There is a clear trend on the heat, flammable gas evolution reactions when comparing reactions of aluminum, magnesium powder and DRI C Fines. The detected trend follows the mathematical function

$$Y = k \times \exp b e \exp (-c x).$$

Where k , b and c constants values are particular for a particular material, this is expected to be so based on the different energies of activation (E_a), threshold temperature, and electric properties.

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