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THE RESULTS PREDICTION OF IRON OXIDES ALUMINOTHERMY

MIHAI OVIDIU COJOCARU[1;2*], TUDOR ANDREI COMAN[3], MIHAI BRANZEI[1], LEONTIN NICOLAE DRUGA[2]

[1]_University POLITEHNICA of Bucharest,313 Splaiul Independenţei,sector 6, 060042,Bucharest, Romania;_
[2]_Romanian Academy of Technical Sciences, Bulevardul Dacia 26, 030167 Bucharest, Romania;_
[3]_QUARK IMPEX S.R.L. Bucuresti, Str. Rasadnitei 121, Sector 6, Bucharest, Romania_
[4]_UTTIS Industries S.R.L., Calea Bucharest 20, Vidra, 077185 Romania_

Abstract. The paper presents the results and conclusions of the statistical processing of data on aluminothermic reduction reactions of iron oxides. Starting from the thermodynamic and chemical information regarding the aluminothermic reduction reactions of the iron oxide mixtures, their thermal and chemical effects were estimated and the information thus obtained was statistically processed. The results obtained by statistical processing of information obtained by theoretical reasons, presented in the form of regression equations or their graphical expressions, can be used to effectively determine the optimal phase composition of thermit kits based on iron oxides and forecast the value of reaction heat, resulting from the actual reactions development. The practical application of these results was ensured by the company QUARK IMPEX SRL, one of the main producers and users of thermit welding kits for rail joints by aluminothermal welding, in Romania.

Keywords: iron oxides; aluminothermy; thermit welding kit; passive experiment method; statistical processing.

1. Introduction

Rigorous control of methalothermic reduction reactions in general and aluminothermic reduction reactions in particular is a challenge for all those who use the process for aluminothermic welding, for example. In the absence of a rigorous control of the thermal effect of the methalothermic reduction reactions, they can

*Correspondence address: cojocarumihaiovidiu@yahoo.co.uk

acquire an explosive character, difficult to control, particularly dangerous [1]. From this point of view, a rigorous dosing of the reactants proportions, the oxide phase and the reducing phase, respectively, and of course, if necessary, the amount of inhibitor introduced into the reaction are requaired in order to slow it down. The composition of thermit powder mixtures includes iron oxides (when in question is the iron-based thermit) widely spreaded in nature, the mineral hematite (Fe_2O_3), respectively magnetite (Fe_3O_4, a double oxide $FeO{\cdot}Fe_2O_3$ with a structure similar to spinels) and wùstite (FeO), a mineral found in meteorites and in native iron or most commonly obtained as a synthetic product, by decomposing iron oxalate in vacuum or by reducing iron trioxide with carbon monoxide [2]. In reality FeO, a nonstoichiometric compound, exists only at pressures higher than 10 GPa [3], and wùstite with a deficit of iron atoms, $Fe_{1-x}O$ ($Fe_{0.99}O$), is unstable below the eutectoid transformation temperature of the Fe-O, about 570 °C. This oxide is stable at temperatures above 570 ºC, below which it decomposes rapidly into Fe_3O_4 and Fe by a disproportionate reaction [3,4]. The presence of metastable wùstite below 570 ºC is supported by the results of many experimental researches [10÷13] and equally contested [14,15]. The metastability of wùstite at temperatures below 570 ºC was mentioned in the eighth decade of the last century by Romanov et.al [10], its occurrence taking place according to the following mechanism:

$$\alpha - Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Wustite \rightarrow \alpha - Fe \tag{1}$$

Pineau et al. [12] confirm through their research the presence of metastable wùstite below 570 ºC, but suggest another mechanism for its appearance, different from the one proposed by Romanov and the team:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow \boldsymbol{(Fe_3O_4 + Fe_{1-x}O)} \rightarrow \alpha - Fe \tag{2}$$

The emergence of metastable wùstite is also supported by researchers in the field of mechanical alloying in which Fe_2O_3 is the main raw material [13]. Graham et al. [14], as well as Rau et al. [15] reached completely different conclusions, carrying out similar experiments to reduce pure hematite. In their experiments, the presence of metastable wùstite was not found. During the combustion of thermit mixtures the appearance of FeO is an undoubted phenomenon. Analysis by electron microscopy and high temperature diffraction of the Fe_2O_3-Al interface (as components of the thermit mixture) [16] revealed the presence of three intermediate zones: ← $FeAl_2O_4$ → ($FeAl_2O_4$ FeO) → FeO ← , arranged between the particle of iron oxide Fe_2O_3 and Al. The appearance of oxyferoaluminide ($FeAl_2O_4$) is conditioned by the presence of FeO and occurs as a result of reactions (3÷5):

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2O_2 \tag{3}$$

$$Fe_3O_4 + 2/3Al = 3FeO + 1/3Al_2O_3 \tag{4}$$

$$FeO + Al_2O_3 \rightarrow FeAl_2O_4 \tag{5}$$

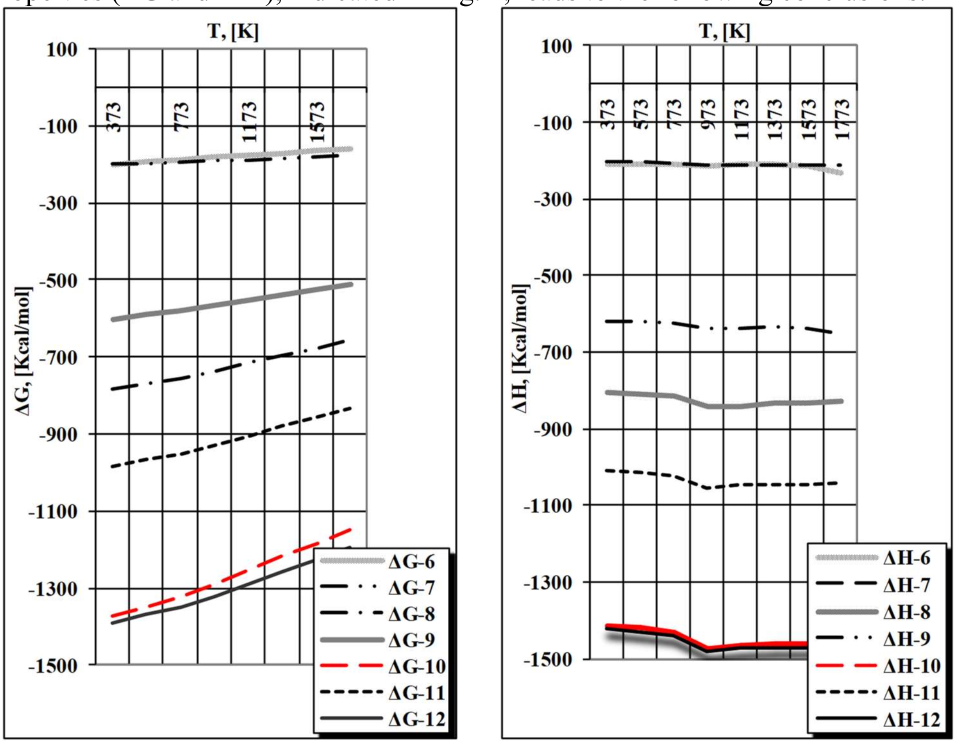
Consequently, the thermit mixtures will contain as iron sources the two stable oxides, Fe_2O_3 and Fe_3O_4, the presence of wùstite in the initial mixtures being possible only after a previous processing of hematite (partial reduction), or by direct reduction of magnetite ($FeO{\cdot}Fe_2O_3$+C → 3FeO+CO ↑). Even under these conditions it is possible to decompose in the range of low temperatures due to its high instability (4FeO → Fe_3O_4+Fe), but, on the other hand, the high speed of the aluminothermic reaction can make possible its direct participation in the reduction reaction.

2. Theoretical solution of the problem in analysis

2.1. Thermodynamics of iron oxides aluminothermic reduction reactions

A hypothetical thermit mixture consisting of the three iron oxides was analyzed in different proportions (the total mass to which the calculations were reported was 10 Kg of oxides), to which was added the reducer - Al powder, thus calculated that In each situation analyzed, the reduction reaction should take place completely (starting from the premise of equilibrium reactions) and the inhibitor (fragments of general purpose carbon steel wire OL37 - about 0.2 %C and 0.85 %Mn), thus dosed that the thermal effect of the reaction can be kept under control.

Analysis of the main chemical reactions (6÷12) that take place between the components of thermal mixtures containing one, two or all iron oxides, together with the metal reducer (Al), and the temperature variation of the main thermodynamic properties (ΔG and ΔH), indicated in Fig. 1, leads to the following conclusions:



a) b)

Fig. 1. Variation of the main thermodynamic properties, depending on temperature: a) ΔG; b) ΔH. The values next to the thermodynamic properties correspond to chemical reactions (6÷12).

- all reactions are thermodynamically possible ($\Delta G < 0$) and occur with heat release ($\Delta H < 0$);
- the highest amounts of heat are released in the presence of magnetite along with wùstite; it is very likely that wùstite will act as an additional source of magnetite ($4FeO \rightarrow Fe_3O_4+Fe$), thus amplifying the overall thermal effect of the aluminothermic reduction reaction.

$$3FeO + 2Al = Al_2O_3 + 3Fe + Q_1 \tag{6}$$

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe + Q_2 \tag{7}$$

$$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe + Q_3 \tag{8}$$

$$3FeO + 2Fe_2O_3 + 6Al = 3Al_2O_3 + 7Fe + Q_4 \tag{9}$$

$$FeO + 5Fe_3O_4 + 14Al = 7Al_2O_3 + 16Fe + Q_5 \tag{10}$$

$$Fe_2O_3 + 3Fe_3O_4 + 10Al = 5Al_2O_3 + 11Fe + Q_6 \tag{11}$$

$$FeO + 4Fe_2O_3 + 2Fe_3O_4 + 14Al = 7Al_2O_3 + 15Fe + Q_7 \tag{12}$$

2.2. Generating the database necessary for statistical processing

Database necessary for statistical processing (Table 1) in order to obtain mathematical models of multiple correlations between the components of thermit mixtures (oxides, reducer, inhibitor), their proportions in mixtures and the results of aluminothermic reduction reactions (oxidation-reduction reactions) , expressed by the amounts of iron, heat and Al_2O_3, was generated by taking into account all the reactions that take place in a hypothetical mixture of 10 Kg of iron oxides (arbitrarily chosen value). The amounts of oxides vary continuously in the six recipes; thus, the amount of Fe_2O_3 varies in the range 0÷7500g, that of Fe_3O_4 in the range 0÷2500g, and that of FeO (synthetic) results from the relationship $FeO=100-\Sigma(Fe_2O_3 + Fe_3O_4)$. We started from the premise that the reactions are in thermodynamic equilibrium (this working hypothesis was adopted to simplify the solution of the problem, accepting at the same time the errors involved). The amounts of reducing agent required for the complete development of the reactions, the amounts of heat released, as well as the amounts of the reaction products, iron and Al_2O_3 respectively, were calculated in this way.
The required inhibitor amount for each recipe (thermit mixture composition) was determined based on the need to limit the reaction temperature to a maximum of 3273 K, estimating the amount of heat resulting from this and the amount of iron; the mass difference between this value and that resulting from the chemical reaction in which the oxides corresponding to the analyzed situation are involved (as type and proportion) represents the very amount of inhibitor necessary for the reaction.

Table. 1. Database required for statistical processing [8]

Components/ Reaction products	**Quantity, [g/*Kcal*]**					
FeO, [g]	0	1000	4000	6400	9000	10000
Fe_2O_3, [g]	7500	6750	4500	2700	750	0
Fe_3O_4, [g]	2500	2250	1500	900	250	0
Al, [g]	3301	3220	2979	2786	2576	2496
Inhibitor (Ol37), [g]	4776	4645	4220	3839	3384	3198
Fe, [g]	*7054*	*7126*	*7341*	*7514*	*7700*	*7772*
Q, [Kcal]	*10952*	*10722*	*10035*	*9485*	*8889*	*8659*
Al_2O_3, [g]	*6256*	*6104*	*5646*	*5280*	*4883*	*4730*

2.3. Statistical processing of data obtained by analytical means

The method of the passive experiment was used (multiple regression analysis) for the statistical processing of the data obtained analytically [17,18]. The correlations between the iron quantities (see Table 2), heat quantity (see Table 3) and Al_2O_3 (see Table 4) and the input parameters (independent variables), represented by the three oxides, the reducer and the inhibitor respectively, were successively analyzed.

2.3.1. Explaining the correlation: Fe [g]=f(FeO;Fe_2O_3;Fe_3O_4;Al;Inh.)

The general database on the aluminothermic reduction process of iron oxide mixtures (Table 1) provided the information for establishing the calculation scheme (Table 2) necessary to determine the system of normal equations with several independent variables, by which it becomes possible to explain the correlation:
Fe [g]=f(FeO; Fe_2O_3; Fe_3O_4; Al; Inh.).

Table. 2. Database and calculation scheme necessary to estimate the iron quantities resulting from the iron oxides mixture aluminothermic reduction reactions: $Fe_{0,99}O$-Fe_2O_3-Fe_3O_4

No.	**Y,** Fe [g]	**X_1** $Fe_{0.99}O$ [g]	**X_2** Fe_2O_3, [g]	**X_3** Fe_3O_4 [g]	**X_4** Al [g]	**X_5** Inh. [g]	**Y^2 x10^7**	**X_1^2 x10^6**	**X_2^2 x10^6**
	1	***2****	***3****	***4****	***5****	***6****	*7*	***8****	***9****
a	**7054**	0	7500	2500	3301	4776	4,97589	0	56.2
b	**7126**	1000	6750	2250	3220	4645	5,07799	10	45.5
c	**7341**	4000	4500	1500	2979	4220	5,38903	16	20.2
d	**7514**	6400	2700	900	2786	3839	5,64602	40,96	7.3
e	**7700**	9000	750	250	2576	3384	5,9290	81	0,56
f	**7772**	10000	0	0	2496	3198	6,0404	100	0
Σ	***44507***	***30400***	***22200***	***7400***	***17358***	***24062***	***33.058***	***238.9***	***129.7***

Continue Table. 2.

No.	**X_3^2 x10^6**	**X_4^2 x10^6**	**X_5^2 x10^6**	**X_1Y x10^6**	**X_2Y x10^6**	**X_3Y x10^6**	**X_4Y x10^6**	**X_5Y x10^6**	**X_1X_2 x10^6**
	10*	***11****	***12****	***13***	***14***	***15***	***16***	***17***	***18****
a	62.5	10.89	22.8	0	52.9	17.6	23.2	33.68	0

b	5.06	10.36	21.57	7.12	48.1	16	22.9	33.1	6.75
c	2.25	8.87	17.8	29.3	33.0	11	21.8	30.9	18
d	0.81	7.76	14.7	48	20.2	6.76	20.9	28.8	17.2
e	0.062	6.63	11.45	69.3	5.77	1.92	19.8	26	6.75
f	0	6.23	10.22	77.7	0	0	19.4	24.8	0
Σ	***14.4***	***50.74***	***98.54***	***231.4***	***159.9***	***53.2***	***128***	***177.2***	***48.7***

Continue Table. 2.

No.	X_1X_3 x10^6	X_1X_4 x10^6	X_1X_5 x10^6	X_2X_3 x10^6	X_2X_4 x10^6	X_2X_5 x10^6	X_3X_4 x10^6	X_3X_5 x10^6	X_4X_5 x10^6
	*19**	*20**	*21**	*22**	*23**	*24**	*25**	*26**	*27**
a	0	0	0	18.7	24.7	35.8	8.25	11.9	15.7
b	2.25	3.22	4.64	15.1	21.7	31.3	7.24	10.4	14.9
c	6	11.9	16.8	6.75	13.4	18.9	4.46	6.33	12.5
d	5.76	17.8	24.5	2.43	7.5	10.3	2.5	3.45	10.69
e	2.25	23.1	30.4	0.18	1.93	2.53	0.64	0.84	8.7
f	0	24.9	31.9	0	0	0	0	0	7.98
Σ	***16.2***	***80.9***	***108.2***	***43.1***	***69.2***	***98.8***	***23.09***	***32.9***	***70.4***

Note: Quantities related to 10 Kg initial iron oxides mixture; $Fe_{0.99}O$ [g] = 10000-Σ(Fe_2O_3+Fe_3O_4)-Table 1)

The data contained in the database (Table 2) generated for modeling the composition variation effects of thermit mixtures on the amount of iron extracted by aluminothermic reduction of iron oxide mixtures allowed the normal equations system (13÷18):

$$6b_0 + 30400b_1 + 22200b_2 + 7400b_3 + 17358b_4 + 24062b_5 = 44507 \tag{13}$$

$$\begin{aligned} &30400b_0 + 238.9\times10^6 b_1 + 48.7\times10^6 b_2 + 16.2\times10^6 b_3 + \\ &+80.9\times10^6 b_4 + 108.2\times10^6 b_5 = 231.4\times10^6 \end{aligned} \tag{14}$$

$$\begin{aligned} &22200b_0 + 48.7\times10^6 b_1 + 129.7\times10^6 b_2 + 43.1\times10^6 b_3 + \\ &+62.9\times10^6 b_4 + 98.8\times10^6 b_5 = 159.9\times10^6 \end{aligned} \tag{15}$$

$$\begin{aligned} &7400b_0 + 16.2\times10^6 b_1 + 43.1\times10^6 b_2 + 14.4\times10^6 b_3 + \\ &+23.09\times10^6 b_4 + 32.9\times10^6 b_5 = 53.2\times10^6 \end{aligned} \tag{16}$$

$$\begin{aligned} &17358b_0 + 80.9\times10^6 b_1 + 69.2\times10^6 b_2 + 23.09\times10^6 b_3 + \\ &+50.74\times10^6 b_4 + 70.4\times10^6 b_5 = 128.0\times10^6 \end{aligned} \tag{17}$$

$$\begin{aligned} &24062b_0 + 108.2\times10^6 b_1 + 98.8\times10^6 b_2 + 32.9\times10^6 b_3 + \\ &+70.4\times10^6 b_4 + 98.54\times10^6 b_5 = 177.2\times10^6 \end{aligned} \tag{18}$$

By solving the system of normal equations, the following solutions are:

$$\boldsymbol{b_0 = 2.1\times10^4;\ \ b_1 = -1.32;\ \ b_2 = -1.86;}$$

$$\boldsymbol{b_3 = 7.47\times10^{-4};\ \ b_4 = 0.57\times10^{-4};\ \ b_5 = -1.086\times10^{-3}}$$

Leading to the following particular form of the regression equation:

$$\begin{aligned}&\boldsymbol{Fe\,[g] = 2.1\times 10^{4} - 1.32\times (Fe_{0.99}O) - 1.86(Fe_2O_3) +}\\&\boldsymbol{+7.47\times 10^{-4}\times (Fe_3O_4) + 0.57\times 10^{-4}(Al) - 1.086\times 10^{-3}(Inh.)}\end{aligned} \tag{19}$$

Where the independent variables $Fe_{0.99}O$, Fe_2O_3, Fe_3O_4, Al, Inh., are in grams.

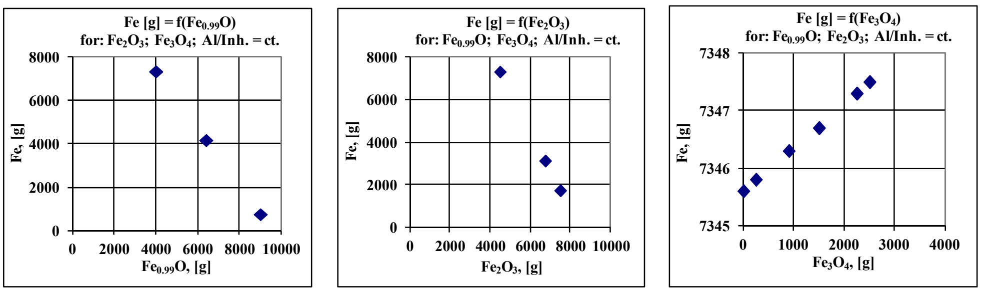
The regression equation (19) allows obtaining with an error of max.+/-0.05 %, the values corresponding to the iron amount resulting from the aluminothermic reduction of a thermit mixture containing 10Kg of iron oxides, provided that the values corresponding to the quantities of oxides, reducing agent and inhibitor to be within the maximum limits of variation mentioned in the database (Table 2).

The regression equation (19) graphical representations are presented in Fig.2, 3, and allow us to understand the parameter variation of interest effects on the quantities and the type of oxides, the amount of reducer and inhibitor, respectively, on the amount of iron extracted.

The regression equation analysis (19) highlights the fact that, in absolute value, the FeO and Fe_2O_3 amounts variation effect is much stronger than that of Fe_3O_4, on the iron extraction efficiency, this being expressed by the iron amount resulting from the aluminothermic reduction reaction.

On the other hand, the negative value of the coefficients related to the quantities of these oxides leads to the conclusion that in order to increase the amount of iron resulting from the aluminothermic reduction it is necessary to decrease their proportions in the initial thermit mixture.

Statistically, the strong effects generated by the variation of the two iron oxides, wùstite and hematite, represent a certainty, but they should not be seen in isolation, strictly individually, but in the general context of the system of which they are part. Keeping all other parameters constant, it is observed that with an increase in the wùstite amount (Fig. 2a) and hematite (Fig. 2b), respectively, the amount of iron resulting from the iron oxides mixture decreases relatively strongly. In reality, the amount of mixture being fixed (10 Kg), the proportion variation of one oxide implicitly determines the others change proportion.



a) b) c)

Fig. 2. Trends in the statistical evolution of the iron amount resulting from the aluminothermic reduction of a iron oxides mixture as a function of the: a) wùstite; b) hematite; c) magnetite ammount; Constant parameters: ***Al-2979 g; Inh.-4220 g***:
a) Fe_2O_3-4500 g; Fe_3O_4-1500 g; b) $Fe_{0,99}O$-4000 g; Fe_3O_4-1500 g; c) $Fe_{0,99}O$-4000 g; Fe_2O_3-4500 g

From the analysis of the isoproperty domains (Fig. 3), it results that the highest amounts of iron resulting from aluminothermic reduction are obtained for mixtures initially poor in hematite and magnetite, but with relatively high contents in wùstite. In the succesion of transformations that the two oxides hematite and magnetite (double oxide of wùstite and hematite), undergo to that of pure iron, wùstite appears in their final stages. In conclusion, the most convenient situation, at a theoretical level, in terms of iron extraction efficiency, would be that in which the initial thermit mixture would have consisted mainly of wùstite. Mixtures with high wùstite contents require relatively small proportions of reducing agent, Al and inhibitor, the reaction thermal effects being relatively low. This last aspect is not convenient if obtaining large amounts of heat is one of the desiderata of the aluminothermic reduction process, as it is in the case of non-removable joints by welding.

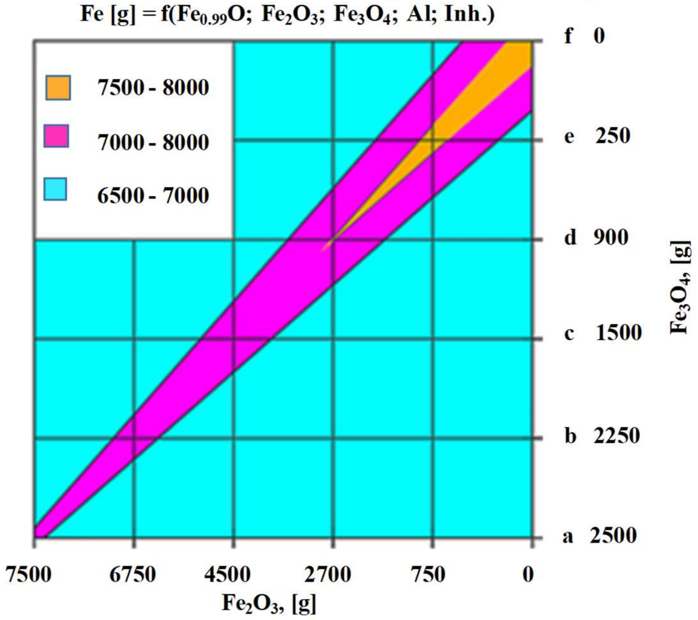


Fig.3 - The *isoproperty domains*, in which the iron amount resulting from the aluminothermic reduction is the same, regardless of how the independent parameters (process variables) are combine.
Note: The fonts on the y-axis correspond to the exact phase compositions of the thermit mixtures, mentioned in Table 1.

2.3.2 Explaining the correlation: Q [Kcal] = f(FeO; Fe_2O_3; Fe_3O_4; Al; Inh.)

Similar to the methodology previously followed (cpt. 2.3.1), from the general analytically established database (see Table 1), was taken on the amounts of heat released by aluminothermic reactions of thermit mixtures containing various proportions of iron oxides and generated the calculation scheme (see Table 3) necessary to determine the system of normal equations with several independent variables. By solving, it becomes possible to explain the correlation
Q [Kcal] = f(FeO; Fe_2O_3; Fe_3O_4; Al; Inh.).

Table. 3. Database and calculation scheme necessary to estimate the amount of heat resulting from the aluminothermic reduction reactions of the iron oxide mixture, $Fe_{0,99}O$-Fe_2O_3-Fe_3O_4.

No.	Y, Q, [Kcal]	Y^2 x10^8	X_1Y x10^6	X_2Y x10^6	X_3Y x10^6	X_4Y x10^6	X_5Y x10^6
	1	*7*	*13*	*14*	*15*	*16*	*17*
a	10952	1.199	0	82.1	27.4	36.1	52.3
b	10722	1,.49	10.72	72.3	24.1	34.5	49.8
c	10035	1.007	40.1	45.1	15	29.9	42.3
d	9485	0.899	60.7	25.6	8.5	26.4	36.4
e	8889	0.791	80	6.66	2.2	22.9	30
f	8659	0.749	86.6	0	0	21.6	27.7
Σ	**58742**	**5.794**	**278.1**	**231.7**	**77.2**	**171.4**	**238.5**

Note: Quantities related to 10 Kg initial iron oxides mixture; $Fe_{0.99}O$ [g] = 10000-Σ(Fe_2O_3+Fe_3O_4)-Table 1);The columns 2,3,4,5,6,8,9,10,11,12,18,19,20...27 are identical to those in the Table 2

The data contained in the database (Table 2.3) generated for modelling the composition variation effects of thermit mixtures on the amount of heat released by iron oxides mixtures aluminothermic reduction allowed the determination of the normal equations system (20÷25):

$$6\times b_0+30400\times b_1+22200\times b_2+7400\times b_3+ \\ +17358\times b_4+24062\times b_5=58742 \tag{20}$$

$$30400\times b_0+238.9\times10^6\times b_1+48.7\times10^6\times b_2+16.2\times10^6 b_3+ \\ +80.9\times10^6 b_4+108.2\times10^6 b_5=278.1\times10^6 \tag{21}$$

$$22200\times b_0+48.7\times10^6 b_1+129.7\times10^6 b_2+43.1\times10^6 b_3+ \\ +62.9\times10^6 b_4+98.8\times10^6 b_5=231.7\times10^6 \tag{22}$$

$$7400\times b_0+16.2\times10^6 b_1+43.1\times10^6 b_2+14.4\times10^6 b_3+ \\ +23.09\times10^6 b_4+32.9\times10^6 b_5=77.2\times10^6 \tag{23}$$

$$17358\times b_0+80.9\times10^6 b_1+69.2\times10^6 b_2+23.09\times10^6 b_3+ \\ +50.74\times10^6 b_4+70.4\times10^6 b_5=171.4\times10^6 \tag{24}$$

$$24062\times b_0+108.2\times10^6 b_1+98.8\times10^6 b_2+32.9\times10^6 b_3+ \\ +70.4\times10^6 b_4+98.54\times10^6 b_5=238.5\times10^6 \tag{25}$$

By solving the system of normal equations, the following solutions are:

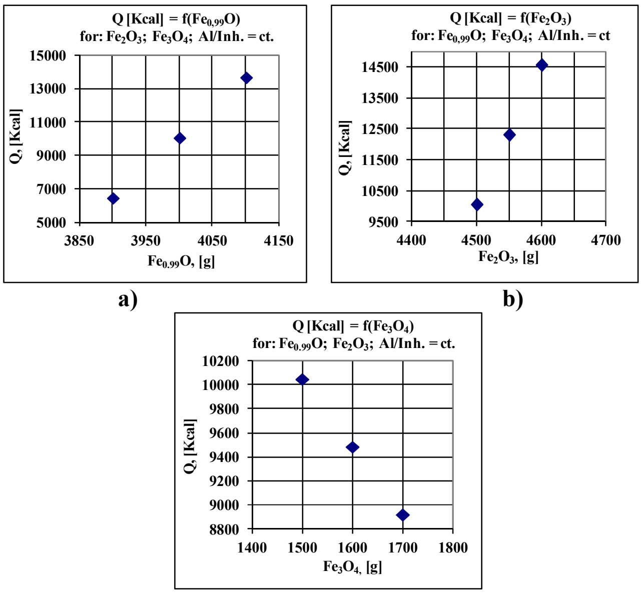
$$\boldsymbol{b_0=-476704;\ b_1=+36.1;\ b_2=+45;} \\ \boldsymbol{b_3=-5.64;\ b_4=+50;\ b_5=-0.15}$$

Leading to the following particular form of the regression equation:

$$\boldsymbol{Q\ [Kcal]=-476704+36.1\times(Fe_{0.99}O)+45\times(Fe_2O_3)-} \\ \boldsymbol{-5.64\times(Fe_3O_4)+50\times(Al)-0.15\times(Inh.)} \tag{26}$$

Where the independent variables $Fe_{0.99}O$, Fe_2O_3, Fe_3O_4, Al, Inh., are in grams.

The equation allows obtaining, with an error of max. +/-1 %, the values corresponding to the amount of heat resulting from the aluminothermic reduction of a thermit mixture containing 10 Kg of iron oxides provide that the values corresponding to the amounts of oxide, reducer and inhibitor to comply with the maximum limits of variation mentioned in the database (Table 1÷3).
The regression equation (26) graphical representations are presented in Fig.4, 5, and allow us to understand the parameter variation of interest effects on the quantities and the type of oxides, the amount of reducer and inhibitor, respectively, on the amount of heat resulting from the aluminothermic reduction reaction of iron oxides.



a) b) c)

Fig. 4. Trends in the statistical evolution of the heat amount resulting from the iron oxides mixture aluminothermic reduction as a function of the: a) wùstite; b) hematite; c) magnetite amount; Constant parameters: ***Al-2979 g; Inh.-4220 g;*** a) Fe_2O_3-4500 g; Fe_3O_4-1500 g; b) $Fe_{0,99}O$-4000 g; Fe_3O_4-1500 g; c) $Fe_{0,99}O$-4000 g; Fe_2O_3-4500 g.

The analysis of the regression equation particular form (26) highlights the effects of the three iron oxides presence on the amount of heat released because of their aluminothermic reduction reaction. Thus, Increasing in wùstite content (Fig. 4a) and more in hematite (Fig. 4b), concomitant with the magnetite content decreasing (Fig. 4c) ensures a substantial increasing in the amount of heat released by the reaction.
The previous analysis, from a thermodynamic point of view, of the iron oxides reducing effects (reactions 6÷12 and Fig.1b), highlighted the fact that the aluminothermic reduction reaction thermal effect of single oxides wùstite and hematite is much lower compared to that resulting from the reduction of magnetite and incomparably smaller than that of the three iron oxides.

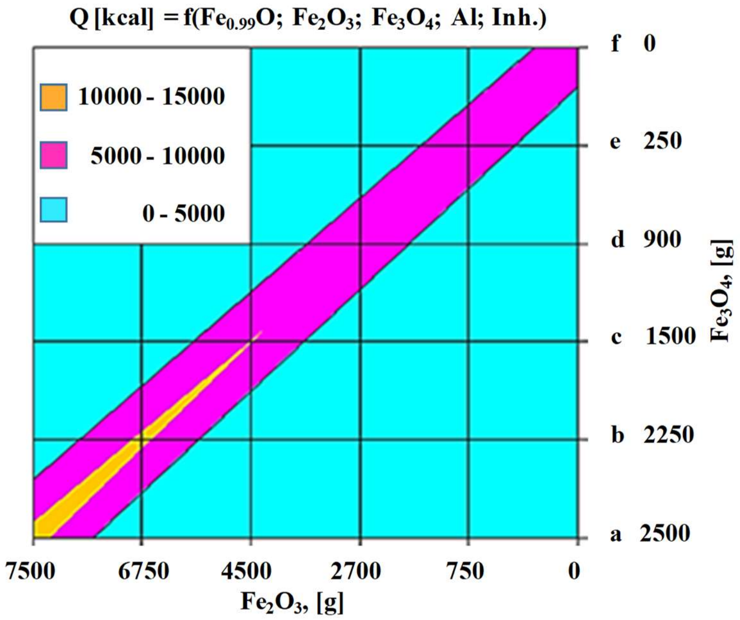


Fig. 5. The *isoproperty domains*, in which the heat amount resulting from the aluminothermic reduction is the same, regardless of how the independent parameters (process variables) are combine.
Note: The fonts on the y-axis correspond to the exact phase compositions of the thermal mixtures, mentioned in Table 1.

The *isoproperty domains* analysis (Fig.5) certifies the thermodynamic conclusions, namely that the highest values of the heat quantities released by the iron oxides aluminothermic reduction reactions are register at high values of hematite and magnetite proportions, respectively relatively low wùstite.

It follows that, for the simultaneous achievement of the two whishes, respectively the highest possible amounts of iron and heat, a compromise solution must be select: depending on the application, we start from required amount of heat needed, and then determine the oxides mixture proportion, thus estimating the amount of iron resulting from the aluminothermic reduction reaction finally.

2.3.3. Explaining the correlation: Al_2O_3 [g] = f(FeO; Fe_2O_3; Fe_3O_4; Al; Inh.)

The calculation algorithm (Table 4) necessary to explain the regression equation *Al_2O_3 [g]=f(FeO; Fe_2O_3; Fe_3O_4; Al; Inh.)* and thus to determine the possibility of estimating the amount of Al_2O_3 resulting from the aluminothermic reduction reactions of iron oxides mixture was established based on the analytically obtained information (Table 1) and the established methodology [17,18].

Table. 4. Database and calculation scheme necessary to estimate the amount of Al_2O_3 resulting from the aluminothermic reduction reactions of the iron oxide mixture, $Fe_{0,99}$ O-Fe_2O_3-Fe_3O_4.

No.	**Y, Al_2O_3, [g]**	**Y^2 x10^7**	**X_1Y x10^6**	**X_2Y x10^6**	**X_3Y x10^6**	**X_4Y x10^6**	**X_5Y x10^6**
	1	*7*	*13*	*14*	*15*	*16*	*17*
a	6256	3.91	0	46,9	15.6	20.6	29.8
b	6104	3.72	6.1	41.2	13.7	19.6	28.3
c	5646	3.18	22.5	25.4	8.47	16.8	23.8
d	5280	2.78	33.8	14.2	4.75	14.7	20.2
e	4883	2.38	43.9	3.66	1.22	12.5	16.5
f	4730	2.23	47.3	0	0	11.8	15.1
Σ	**32899**	**18.2**	**153.6**	**131.3**	**43.7**	**96**	**133.7**

Note: Quantities related to 10 Kg initial iron oxides mixture; $Fe_{0.99}O$ [g] = 10000-Σ(Fe_2O_3+Fe_3O_4)-Table 1); The columns 2,3,4,5,6,8,9,10,11,12,18,19,20...27 are identical to those in the Table 2.

The data contained in the database (Table 1÷4) generated for modeling the composition variation effects of thermit mixtures on the amount of Al_2O_3 extracted by aluminothermic reduction of iron oxide mixtures allowed the determination of the normal equations system (27÷32):

$$6\times b_0+30400\times b_1+22200\times b_2+7400\times b_3+ \\ +17358\times b_4+24062\times b_5=32899 \tag{27}$$

$$30400\times b_0+238.9\times10^6 b_1+48.7\times10^6 b_2+16.2\times10^6 b_3+ \\ +80.9\times10^6 b_4+108.2\times10^6 b_5=153.6\times10^6 \tag{28}$$

$$22200\times b_0+48.7\times10^6 b_1+129.7\times10^6 b_2+43.1\times10^6 b_3+ \\ +62.9\times10^6 b_4+98.8\times10^6 b_5=131.3\times10^6 \tag{29}$$

$$7400\times b_0+16.2\times10^6 b_1+43.1\times10^6 b_2+14.4\times10^6 b_3+ \\ +23.09\times10^6 b_4+32.9\times10^6 b_5=43.7\times10^6 \tag{30}$$

$$17358\times b_0+80.9\times10^6 b_1+69.2\times10^6 b_2+23.09\times10^6 b_3+ \\ +50.74\times10^6 b_4+70.4\times10^6 b_5=96\times10^6 \tag{31}$$

$$24062\times b_0+108.2\times10^6 b_1+98.8\times10^6 b_2+32.9\times10^6 b_3+ \\ +70.04\times10^6 b_4+98.54\times10^6 b_5=133.7\times10^6 \tag{32}$$

By solving the system of normal equations, the following solutions are:

$$\boldsymbol{b_0=+29458.6;\ b_1=-3.3;\ b_2=-5.02;}$$

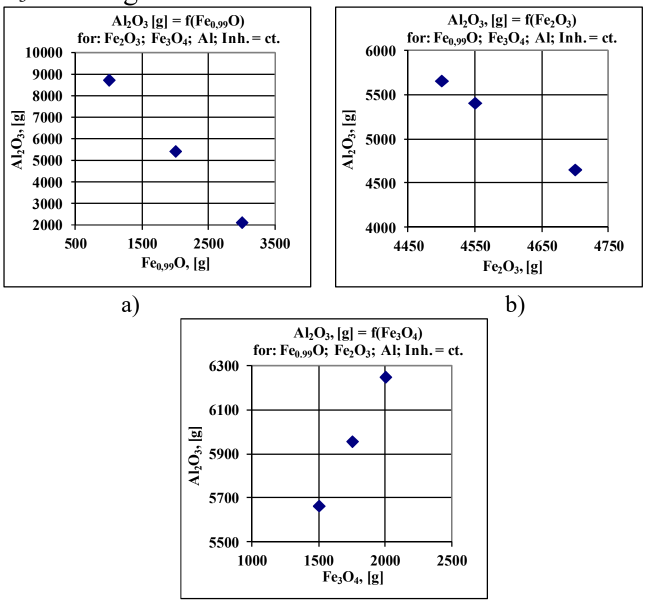
$$\boldsymbol{b_3=+1.17;\ b_4=+2.29;\ b_5=+0.81}$$

Leading to the following particular form of the regression equation:

$$\boldsymbol{Al_2O_3\ [g]=29458.6-3.3\times(Fe_{0.99}O)-5.02\times(Fe_2O_3)+ \\ +1.17\times(Fe_3O_4)+2.29\times(Al)+0.81\times(Inh)} \tag{33}$$

Where the independent variables $Fe_{0.99}O$, Fe_2O_3, Fe_3O_4, Al, Inh., are in grams.

The equation allows obtaining, with an error of max. +/-5 %, the values corresponding to the amount of (Al_2O_3) resulting from the aluminothermic reduction of a thermal mixture containing 10 Kg of iron oxides, provided that the values corresponding to the amounts of oxide, reducer and inhibitor to comply with the maximum limits of variation mentioned in the database (Table 1÷3).
The regression equation (33) graphical representations are presented in Fig. 5, 6, and allow us to understand the parameter variation of interest effects on the quantities and the type of oxides, the amount of reducer and inhibitor, respectively, on the amount of Al_2O_3 resulting from iron oxides aluminothermic reduction reactions.



a) b)

c)

Fig. 6. Trends in the statistical evolution of the corundum (Al_2O_3) amount resulting from the iron oxides mixture aluminothermic reduction as a function of the: a) wùstite; b) hematite; c) magnetite amount; Constant parameters: ***Al-2979 g; Inh.-4220 g;*** a) Fe_2O_3-4500 g; Fe_3O_4-1500 g; b) $Fe_{0,99}O$-4000 g; Fe_3O_4-1500 g; c) $Fe_{0,99}O$-4000 g; Fe_2O_3-4500 g.

The regression equation analysis (33) reveals similarities regarding the effects of the iron oxides proportions variation in the thermit mixture on the way in which the synthesis yield of Al_2O_3 and the iron extraction efficiency are influence, consequently to develop of the aluminothermic reaction. Thus, by increase, the wùstite proportion (Fig. 6a) and hematite (Fig. 6b) in the initial mixture, the iron, and Al_2O_3 amounts in the final reaction products decreasing.
The *isoproperty domains* analysis (Fig.7) leads to the conclusion that high values of Al_2O_3 content (between 4,000 g and 6,000 g) are obtained in a relatively wide range of the three oxides proportions in the thermit mixture. The amount of Al_2O_3 generated by the iron oxides aluminothermic reduction reaction is strictly dependent on the reducer amount, Al (see Fg.8), but also on the oxygen amount provided by oxides during their reduction process.

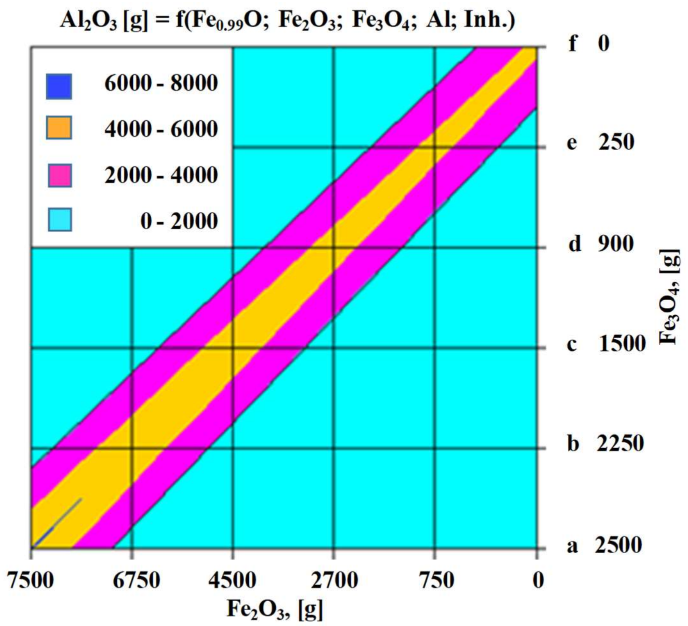


Fig. 7. The *isoproperty domains*, in which the Al_2O_3 amount resulting from the aluminothermic reduction is the same, regardless of how the independent parameters (process variables) are combine. *Note: The fonts on the y-axis correspond to the exact phase compositions of the thermal mixtures, mentioned in Table 1.*

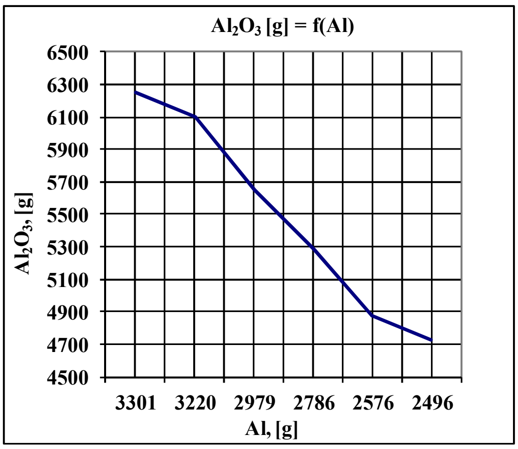


Fig. 8. Dependence of the amount of Al_2O_3 generated by the iron oxides aluminothermic reduction on the amount of Al-reducer, which can be calculate with the relation: $Al_2O_3 = 0.785+1.895 \cdot Al$.

2.4. Conclusions resulting from the statistical processing of the obtained analytically data

The statistical processing of the obtained analytically data results, are of great interest both from a theoretical and practical point of view.
Theoretically, because they allow understanding how the different components of the thermit mixture influence the development of the aluminothermic reduction reaction itself and in this way, depending on the needs, how their proportion must be modifies to influence the reaction in the desired direction.
Practically, because by quantifying the influence effects of the mixture components it becomes possible to conduct the reaction in the desired direction without prior probing.

3. Practical verification of mathematical models obtained by statistical processing of analytical information

The practical verification of the variation effects of the thermit mixtures composition (iron thermit) on the results of their aluminothermic reduction reaction was performed within the company S. C. QUARK IMPEX S.R.L., in order to validate the solutions resulting from statistical processing of analytically obtained information.

3.1. Materials and equipment used in practical proofing

Natural iron oxides, hematite, magnetite, and synthetic wùstite (obtained by reducing hematite with carbon monoxide) with granulations within the limits of 0.2-1.5 mm, were use to verify the conclusions resulting from the statistical processing of the data analytically obtained. Aluminum powder obtained by air spraying (ALCOA process), with granulations in the range of 150-500 μm, was used as reducing agent, and OL37 steel wire as an inhibitor of the reaction.
The reaction was carried out in the air, or in a calorimeter (when the thermal effect of the reaction was estimated), the thermit kit weighing 200g (components rigorously mixed in bi-tronconical mixer for 30 min), and the reaction was primed resistively.
The iron amount determination, respectively Al_2O_3 resulting from the reaction was performed by analytical balances.

3.2. Quark Diagram / Chart

The series of thermal mixtures with compositions in the field of those mentioned in Table 1 have been taking into analysis, the aluminothermic reduction reactions was initiated, and their results were verified. The experimentally results, corroborated with those obtained by statistical processing of analytically estimated data, allowed the construction of a diagram / chart of immediate practical utility, as is shown in Fig. 9. Thus, starting from the amount of heat required for a certain application, the iron and Al_2O_3 amounts resulting from the reaction (relative to 10 Kg of initial oxides mixture: $Fe_{0.99}O$, Fe_2O_3, and Fe_3O_4), can be estimate. By drawing a horizontal line, that goes through the value of the desired amount of heat, being determined in this way, at the ordinates intersections corresponding to these components, the value of interest. Subsequently, in order to specify the actual amounts of oxides in the mixture, the aluminum and inhibitor amount (the thermit mixture recipe) necessary to ensure the respective heat amount, continue horizontally line until the intersection of the graphical dependence (an inclined line) and make the projection of this point of intersection on the four abscissas.

Practically (from the diagram / chart), in order to obtain 10,035 Kcal, the diagram shows that a thermit mixture kit should contain 4,000 g of wùstite, 4,500 g of Fe_2O_3 1,500 g Fe_3O_4 (per 10 Kg oxide mixture), 2,979 g of Al and 4,220 g of inhibitor. Analytically, using the regression equation (26), it results that such a thermit mixture kit produces because of the aluminothermic reduction reaction 10,053 Kcal. Between the two values obtained using the two ways of estimation, the error is below 2 %, a level that is consider extremely satisfactory.

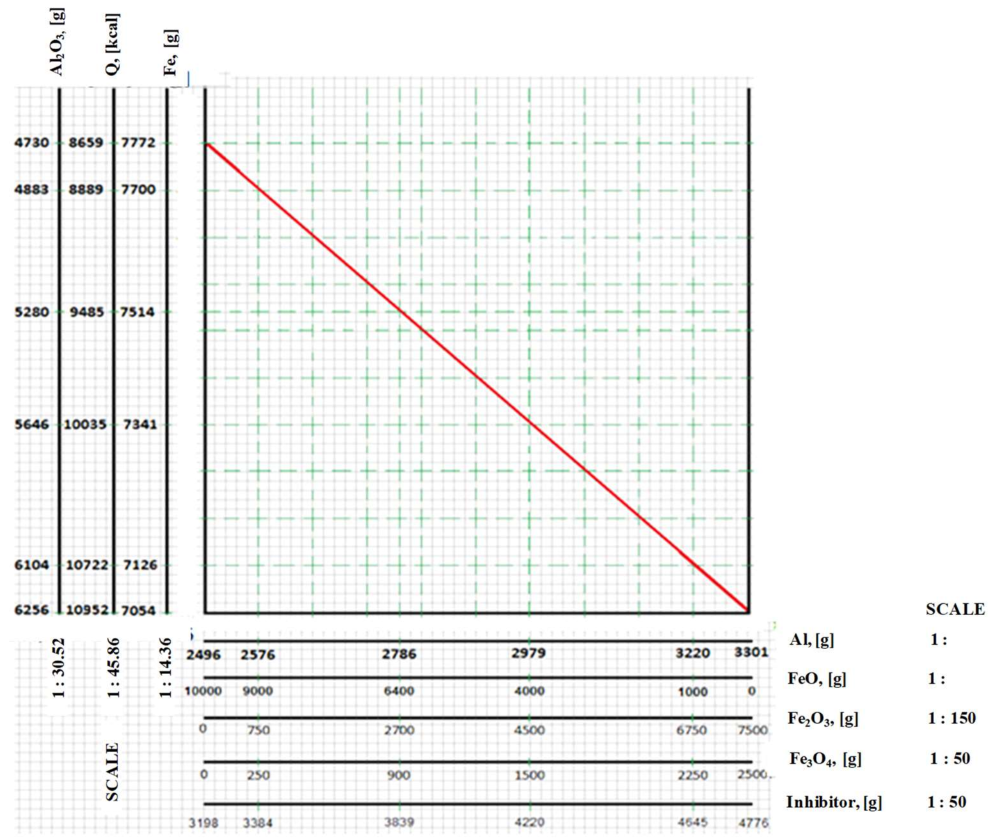


Fig. 9. Quark Diagram / Chart

3.3 Conclusions from experimental results

The results of the experimental verifications materialized in the Quark Diagram / Chart, once again confirmed the validity of the solutions obtained by statistical processing of the analytically obtained data and created a useful tool available to those who prepare thermit kit mixtures with strictly specified destination, so that depending on requirements efficiently modify (without prior probing), their phase composition.

4. Conclusions

i. Mathematical models of the interactions between the components of thermit mixtures and the results of the aluminothermic redox reactions, expressed in the form of regression equations, are useful tools in the hands of those who actually use these processes, for example in order to achieve non-removable joints by welding.
ii. The particular forms of these regression equations, obtained for the case of iron thermit (iron oxides mixtures, Al powder and OL37 steel wire), by statistical processing of analytically obtained data, led to experimentally validated solutions within S.C. QUARK IMPEX S.R.L., and very close (error below 2 %) to the solutions obtained by the company, using its own diagrams.
iii. The mathematical model of the interaction between the composition of the thermit kits and the results of the aluminothermic reactions offers the users an additional opportunity to those offered by the Quark Diagram / Chart. This consists in the possibility to determine quickly how the absence of an oxide in the composition of the thermit mixture can be partially or totally compensate, without altering the level of the results obtained after the aluminothermic reduction reaction.

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