



ENVIRONMENTAL ISSUES REGARDING THE INDUSTRIAL AREAS WITH PULVEROUS FERROUS WASTES

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ABSTRACT

Administering the wastes should represent a problem of strategy in the internal practice of company, taking into account the following objective: reducing the quantity of secondary products to the minimal level; minimizing the quantity of secondary products obtained from a technological process through recycling; increasing the economic fields degree of recovery (transforming wastes in useful sub products; handling the problems with a negative impact on the environment when treating and transporting wastes, through supervising and control.

Possibilities of recovering pulverous ferrous wastes and re – introducing them in iron industry, considering that on a national levels this activity has, unfortunately, a very restricted area. Taking into account the above mentioned aspects, we have conducted research and study on the following ferrous powdery wastes: Siemens – Martin's steel plant dust, electric steel plant dust, sintering sludge, siderite waste and red mud product by Aluminum plant – Oradea, limestone dust (obtained through gas-purification in limestone plants) and grinding blast furnace slug have been also used.

A number of 8 technological models with 5 recipes for each model have been made and experimented. For 4 of the models the roughness of the pellets obtained has been done through burning and for the other 4 it has been obtained on cold conditions. After the process of roughness the quality characteristics (chemical, and granulometric composition, compression resistance), the reducibility degree as well as the oxygen reduction and using degree, have been established. The components used for the experimental recipes have varied as follows: 30-95% steel plant dust; 0-11% coke slime; 0-32% siderite waste concentrate; 0-65% limestone dust; 0-2% dolomite dust; 0-5% fluorine; 0-7% cement; 0-4% blast furnace slug; 0-3% bentonite; 0-4% coal dust; 0-7% red silt. Variation in large limits of the components had been determined a large limits of variation for the chemical composition: 39,95-55,29% Fe_{tot} , 1,03-4,98% FeO ; 51,23-72,66% Fe_2O_3 ; 3,49-8,87% SiO_2 ; 4,83-10,69% CaO ; 2,54-9,81% Al_2O_3 . We should also mention that for the same recipe, there were no great variations of the chemical composition.

The experiments have proved the fact that the studies wastes can be processed through palletizing and can be used in the siderurgical industry. The palletizing recipe will be chosen according to the necessary aim for the metallurgical slag: it can be either an early producing of an active slag (oxidant and basic).

Processing the ferrous pulverous wastes is worth doing taking into account the price of the iron raw materials on the world market, as well as the expenses for ecologizing the environment.

1. INTRODUCTION

In the last decade, manufacturing technologies for metallic materials all over the world have reached a high performance level, demonstrating a high capacity to adapt to the changes due to conditions imposed on raw materials and energy, necessary to increase productivity and decrease specific use, as well as obeying to stricter environmental regulations. The remarkable results obtained in modern iron factories were possible through implementation of management systems into industrial activity, systems which imposed the analysis, evaluation and selection on changes at the level of technologies / equipments, respectively alternative technologies, from the perspective of its specific instruments, among which one of the most complex is undoubtedly the life cycle analysis (LCA). LCA (from Life Cycle Analysis) appeared as a result of society's concern for the quality of environmental factors and the obligation of governmental institutions to control the phenomenon of industrial pollution.

The administration of secondary materials must represent a problem of strategy in the internal practice of the company, taking into account the following objectives: reducing to the minimal level the quantity of secondary products; minimizing through recycling the quantity of secondary products obtained from a technological process; increasing the degree of recovery (transforming wastes in useful subproducts for other sectors of economy); dominating through supervising and control of problems with a negative impact upon the environment, that can occur when treating and transporting wastes.

2. EXPERIMENTS AND RESULTS

Based on the above, we performed a study regarding the possibilities of recovery pulverous ferrous wastes in iron industry, considering that on a national level this activity has, unfortunately, a very restricted area. For this we'll refer to pulverous ferrous wastes, which are in Hunedoara and for whom, in first phase, was determined the chemical (table 1) and granulometrics composition (table 2).

Both chemical and granular composition it were determined on 5 samples taken from different zones (according to the norms) and it have been calculated the average values presented in tables.

Analysis the granulometrics composition resulted the best process wastes technology pelletizing. especially if it is taken into account the use of pellets at steel plant.

Within the framework of this technology it will be performed and experimenting, the following operations:

- The supply with raw and auxiliaries materials from companies which have ferrous wastage and respectively binders. The storage of raw materials is made in separate silos.
- The determination of chemical and granular composition for the material that will be processed. The granular ratio bigger than 1mm it

shouldn't exceed 10%. If the iron content is less than 30% in the sintering sludge than it will be reduce with 2% the proportion of sinter in the pelletizing charge and in the same manner it will increase the proportion of steel plant dust.

- The materials are dosed according to the established recipe for a pelletizing charge of 40kg.
- After dosing, the materials are introduced in the homogenizing drum, the time for this operation being 10 minutes.
- After homogenizing the material (40kg material/charge) is introduced in the pelletizing equipment.
- The duration for the pelletizing operation is 25-30 min. On the entire duration of the process it needs to watch over the wetting manner of the charge and the formation of the pellets. Function of the material humidity. the water discharge is adjusted.
- After finishing of the pelletizing operation. the obtained pellets are subjected to granular sorting operation. The granular ration under 10mm is reintroduced in the circuit (in the pelletizing flux) and the granular ratio bigger than 10mm will be subjected to hardening. The coldbinder hardening is made by maintaining the materials in the hot air blast for minimum 7 days or in silo for 14 days.
- The burning hardening is made in electric furnaces or in flame furnaces, according to heating diagram.
- After hardening, the pellets are subjected again to granular sorting operation. the granular ratio bigger than 10 mm being sent to the customer and the granular ratio under 10 mm being reintroduced in the circuit.
- Each pellets batch it's accompany by an quality certificate that contain: chemical composition, (%); granular composition, (%); compressive strength, (daN/pellet).

TABLE 1. CHEMICAL COMPOSITION OF PULVEROUS WASTES AND OF USED BINDING ADDITION

MATERIAL	Fe _{tot} [%]	FeO [%]	Fe ₂ O ₃ [%]	SiO ₂ [%]	Al ₂ O ₃ [%]	CaO [%]	MgO [%]	MnO [%]	P ₂ O ₅ [%]	S [%]	Zn [%]	P [%]	C [%]	Others [%]
SM's steel plant dust	57.45	3.43	78.26	3.27	1.24	4.71	2.20	4.20	0.72	0.32	0.47			1.17
Electric steel plant dust	53.67	2.98	73.37	3.49	1.07	5.11	2.34	4.80	0.74	0.34	0.84			4.92
Sintering sludge (before drying)	24.41	7.14	26.93	8.30	7.48	8.39	1.98	0.72	-	1.10	-	0.11	17.66	20.20
Sintering sludge (after drying)	30.40	8.84	33.61	10.35	9.33	10.47	2.47	0.89	-	1.38	-	0.13	22.04	1.27
Siderite wastes	10.75	6.91	7.68	34.77	2.93	16.81	6.78	1.37	-	-	-	-	-	22.76
Siderite concentrate	20.95	9.96	18.85	19.87	3.19	20.81	7.42	2.24	-	-	-	-	-	17.65
MATERIAL USED FOR BINDING ADDITION														
Limestone dust	0.35	-	0.5	0.8	0.45	96.3	1.3	0.35	-	0.1	-	0.2	-	-
Blast furnace slug	0.25	0.33	-	40.3	8.25	40.52	7.17	1.11	-	-	-	-	-	2.32

TABLE 2. GRANULOMETRIC COMPOSITION OF THE MATERIALS

MATERIAL	GRANULOMETRIC CLASSES, [%]						
	< 63 µm	63-100 µm	100-250 µm	250-500 µm	500-710 µm	710-1000 µm	> 1000 µm
Siemens Martin steel plant dust	55.12	12.11	10.45	8.07	7.41	6.84	0
Electric steel plant dust	60.11	10.28	8.43	7.52	6.81	6.85	0
Sintering sludge	46.26	18.31	15.65	8.12	6.45	3.21	2
Siderite wastage concentrate	42.16	21.18	12.48	10.13	6.42	4.29	3.34
Red mud	54.17	15.82	12.13	7.41	7.36	3.18	0
Limestone dust	65.21	19.71	5.82	4.13	3.10	2.03	0
Dolomite dust	56.11	25.6	7.41	5.11	3.06	2.71	0
Fluorine	13.45	23.15	20.31	17.26	8.41	7.15	10.27
Blast furnace slug	31.14	25.12	15.36	12.13	8.46	6.89	0.9
Bentonite	47.12	23.25	15.41	7.02	4.08	3.12	0
Coke dust	32.62	26.43	12.36	7.84	6.51	5.41	8.83

TABLE 3. PERCENTAGE COMPOSITION OF RECIPES

Recipe component. [%]	MATERIAL											
	Steel plant dust (SM+OE)	Sintering sludge	Siderite wastage concentr.	Red mud	Limestone dust	Dolomite dust	Flu-rine	Cement	Blast furnace slug	Bentonite	Coke dust	Power plant ash
A	1	86	11	-	-	-	-	-	-	3	-	-
	2	88	10	-	-	-	-	-	-	2	-	-
	3	90	7.5	-	-	-	-	-	-	2.5	-	-
	4	92	5	-	-	-	-	-	-	3	-	-
	5	95	2	-	-	-	-	-	-	3	-	-
B	1	80	6	-	-	-	-	6	4	-	4	-
	2	81	4	-	-	-	-	6	5	-	4	-
	3	82	3	-	-	-	-	7	4	-	4	-
	4	84	2	-	-	-	-	7	3	-	4	-
	5	90	-	-	-	-	-	5	5	-	-	-
C	1	80	-	12	-	3	2	-	-	3	-	-
	2	82	-	10	-	3	2	-	-	3	-	-
	3	84	-	9	-	2	2	-	-	3	-	-
	4	86	-	8	-	2	1	-	-	3	-	-
	5	91	-	4	-	1	1	-	-	3	-	-
D	1	70	10	6	-	-	-	6	4	-	4	-
	2	75	5	5	-	-	-	6	5	-	4	-
	3	80	-	-	5	-	-	7	4	-	4	-
	4	85	-	-	2	-	-	7	3	-	3	-
	5	90	-	-	-	-	-	5	5	-	-	-
Recipe component. [%]	Steel plant dust (SM+OE)	Sintering sludge	Siderite wastage concentr.	Red mud	Limestone dust	Dolomite dust	Flu-rine	Cement	Blast furnace slug	Bentonite	Calcite dust	Power plant ash
E	1	80	-	-	7	4	1	-	-	3	2	3
	2	80	-	-	8	4	1	-	-	3	2	2
	3	83	-	-	5	4	1	-	-	3	2	2
	4	87	-	-	-	4	1	-	-	3	2	3
	5	90	-	-	-	4	1	-	-	3	2	-
F	1	75	-	-	10	4	1	-	6	2	-	2
	2	78	-	-	7	4	-	-	7	1	-	3
	3	80	-	-	3	4	2	-	7	-	-	2
	4	82	-	-	3	4	2	2	6	2	-	1
	5	85	-	-	-	2	1	-	7	1	-	4
G	1	30	-	-	-	70	-	-	-	-	-	-
	2	30	-	3	3	60	-	-	-	2	-	2
	3	30	2	3	3	60	-	-	-	2	-	-
	4	33	-	-	-	60	-	5	-	2	-	-
	5	35	-	-	-	60	-	-	-	2	3	-
Recipe component. [%]	Steel plant dust (SM+OE)	Sintering sludge	Siderite wastage concentr.	Red mud	Limestone dust	Dolomite dust	Flu-rine	Cement	Blast furnace slug	Bentonite	Calcite dust	Power plant ash
H	1	50	-	40	-	-	-	7	1	2	-	-
	2	52	-	33	5	2	-	6	2	-	-	-
	3	55	-	35	-	2	-	7	1	-	-	-
	4	57	-	30	-	3	2	-	6	2	-	-
	5	60	-	30	-	-	2	-	6	2	-	-

The recipes for the experimental variants (A, B, C, D, E, F, G, H) are presented in table 3. Within the framework of every technological variant it have been produced 5 pellets charges for each recipe (40 kg/charge; 200 kg/recipe; 1000 kg/variant). For each variant it have been determiner the quality defined by chemical composition (table 4), granular composition and compressive strength (for 10 pellets / recipe) – table 5.

TABLE 4. VARIATION OF CHEMICAL COMPOSITION

Recipes	Variation of chemical composition. [%]													
	Fe _{tot}	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	P ₂ O ₅	S	Zn	C	CaF ₂	Others
A	52.86-55.29	3.44-3.92	71.15-75.17	3.46-4.10	3.72-4.64	4.83-5.35	2.14-2.18	3.71-4.01	0.65-0.69	0.22-0.32	0.40-0.45	0.44-2.42	0	1.15-1.24
B	47.76-51.72	3.07-3.29	64.62-70.43	5.91-6.58	3.03-3.73	8.52-8.96	2.11-2.34	3.46-3.84	0.59-0.65	0.18-0.24	0.38-0.42	0-5.28	0	1.19-1.29
C	45.58-49.80	3.11-3.58	61.14-67.69	4.14-5.37	3.66-3.81	7.13-10.69	2.80-3.52	4.12-4.46	0.61-0.68	0.28-0.31	0.67-0.76	0	0	5.26-6.20
D	41.88-48.32	2.40-3.58	55.85-66.03	6.13-7.78	2.88-4.00	8.83-10.19	2.22-2.62	3.63-4.38	0.55-0.67	0.27-0.38	0.59-0.76	0-6.16	0	3.89-4.74
E	49.10-53.27	2.99-3.55	66.30-72.66	4.58-5.94	1.86-4.51	7.73-9.02	2.90-3.34	3.55-3.69	0.58-0.65	0.16-0.18	0.38-0.42	0	0	1.99-3.31
F	45.50-46.83	2.92-3.57	61.04-63.45	5.74-7.43	1.64-3.30	7.70-9.45	2.56-3.43	3.39-3.57	0.55-0.62	0.15-0.18	0.35-0.40	0	5.70-6.65	1.57-6.60
G	41.95-44.18	1.03-1.66	58.15-61.98	7.94-8.76	7.81-9.81	5.61-8.61	1.36-2.59	1.26-1.49	0.22-0.26	0.06-0.11	0.14-0.16	0-0.66	0	10.33-12.16
H	39.95-41.67	4.61-5.20	51.23-54.30	5.77-8.92	4.16-5.68	7.13-9.07	2.09-2.42	2.49-2.79	0.48-0.53	0.54-0.65	0.24-0.28	6.61-8.42	5.70-6.65	0.10-3.70

Table 5. GRANULOMETRIC COMPOSITION AND COMPRESSIVE STRENGTH OF THE PELLETS

Pellets produced after recipes	< 10mm	10-15mm	> 15mm	Average compressive strength, [daN/pellet]	
A	1	3.50	92.20	4.30	170
	2	2.80	93.50	3.70	185
	3	2.40	93.10	4.50	175
	4	2.90	93.30	3.80	204
	5	3.10	92.80	4.10	210
B	1	1.70	93.20	5.10	215
	2	1.80	92.00	6.20	220
	3	1.50	92.20	6.30	215
	4	1.65	92.00	6.35	210
	5	1.75	92.60	5.65	190
C	1	2.90	92.90	4.20	185
	2	3.20	92.10	4.70	215
	3	2.70	93.50	3.80	195
	4	2.40	92.10	4.50	205
	5	3.10	92.60	4.30	200
D	1	1.80	93.00	5.20	220
	2	2.10	92.80	5.10	225
	3	1.75	91.95	6.30	215
	4	2.20	92.00	5.80	200
	5	1.90	91.70	6.40	210
E	1	3.4	94.2	2.4	189
	2	2.8	94.6	2.6	194
	3	2.7	94.6	2.7	195
	4	2.56	93.94	3.5	203
	5	2.45	93.75	3.8	186
F	1	2.4	93.3	4.3	200
	2	2.3	93.02	4.68	210
	3	2.35	92.85	4.8	204
	4	2.6	92.2	5.2	215
	5	2.4	92.2	5.4	218
G	1	3.1	93.1	3.8	190
	2	2.7	93.1	4.2	195
	3	2.8	92.6	4.6	186
	4	2.6	92.6	4.8	194
	5	2.45	93.05	4.5	199
H	1	3.8	91.7	4.5	175
	2	3.4	92.3	4.3	170
	3	3.12	92.76	4.12	178
	4	2.9	93.2	3.9	181
	5	2.87	93.38	3.75	176

The industrial testing was made using, in first phase. a direct heating furnace having the capacity 5 tones. Pellets addition had the purpose to replace partially (25%) the iron ore used for decarbonisation. Thereby, from total addition 4.2 kg/100kg (steel). The iron ore was replaced 1.05 kg with an equivalent of 1.2 kg of pellets (it was calculated for iron equivalent, respectively oxygen), which demand a specific addition of 12kg/t that means 60kg/charge.

From the performed determinations regarding the oxygen consumption used for carbon oxidation it resulted that mean utilisation grade of oxygen was between 73...77% (table 6). Also it was observed that in case of using the pellets produced after the recipes 5B and 5D it wasn't produced skimming. Because these pellets does not contain the components which produce skimming (C from it's burning result CO and CO₂ and respectively carbonates from which decomposition result CO₂).

A good skimming was obtained in case of using the pellets produced after the recipes 1A, 2A, 1D and 3A. These having as foamer the carbon from lime residue, and recipe 1D and the coke dust and the siderite concentrate, which lead to the best skimming.

An acceptable skimming was observed in case of utilisation of pellets produced after the recipes 4A, 1B, 2B, 3B, 4B and 2D. The recipes 4A, 1B and 2B had as skimming component the carbon and the last recipe (2D) had in it's composition carbonates (concentrate of siderite waste). A slightly skimming was observed for recipes having small content of foamer elements (5A. 1C. 2C. 3C. 4C. 3D. 4D).

TABLE 6. OXYGENE UTILISATION GRADE, [%]

RECIPE	VARIANT			
	A	B	C	D
1	74.56	75.26	76.47	75.14
2	76.23	77.13	73.28	76.18
3	73.17	74.18	77.04	73.24
4	77.08	73.02	76.12	76.95
5	75.15	72.96	74.15	75.37
Media	75.238	74.51	75.412	75.376

Next, we'll go to experiments the E, F, G and H variants, in an electric furnace having the capacity 100t. Pellets produced after the recipes 5E, 1F, 2F, 3F, 4F, 5F, 1G, 3G, 4G and 5G have been introduced in the first dipper in quantity of 0.2% from weight of the charge (replacement grade with ore 1: D for variant E and F. and 3kg pellets at 1kg ore and 1.5kg pellets at 1kg limestone).

Pellets produced after the recipes 1E, 2E, 3E, 4E, 2G, 1H, 2H, 3H, 4H and 5H have been introduced in the second dipper (with replacement index 2kg pellets at 1kg ore and 3.5kg pellets at 1kg limestone for variant H).

TABLE 7. OXYGEN UTILISATION GRADE, [%]

RECIPE	VARIANT			
	E	F	G	H
1	75.18	76.83	76.12	76.83
2	76.26	77.02	74.82	75.29
3	77.14	75.18	75.36	75.26
4	75.65	76.25	73.91	74.18
5	76.34	75.16	76.24	75.36
Media	76.114	76.088	75.29	75.384



FIGURE 1. PELLETIZING EQUIPMENT



FIGURE 2. ELECTRIC FURNACES



FIGURE 3. PELLETS

3. CONCLUSION

The observations obtained throughout the experiments, several the followings:

- the obtain results after the analysis shows that refuse process like pellets after A. B. C and D recipes can be practice valorificated, pellets recipe is chosen in degree of slag foaming;
- when using pellets obtained according to the 1E, 2E, 3E, 4E and 2 recipes a very slight foaming was noticed as a result of a small quantity of carbon brought by power plant ash;
- when using pellets produced according to the G recipes an early making of an active slag (oxidizing or basic) resulted;
- a similar behaviour was noticed at the pellets produced according to the H recipes and in addition a slight foaming of the slag, generated by carbonated dissociation.

So, we can state that the pellets worked well and they can be reintroduced in the economic circuit (the process refuse like pellets can be exploited in the siderurgical field). Like the forth recipes, in this case we are going to choose the pellets recipe (for example. to hurry the forming process of an active slag. will choose the G recipe).

The processing becomes profitable from ecological point of view it we take in account expenses for environment ecology. In a metallurgical company, operationally closed, the expenses for ecology reach the average value of 50000 €/ha (approx. 10000000 €/140ha). The dust taken in account in order to be processed fills a area of approx 5ha. If we take in account that the price of ore fines (hematite India with iron content of 62%) reach in the third quarter of 2004 year at a medium price of 25...30\$/t (that means for steel plant dust 20...30\$/t). It become profitable the processing of these wastes even in the case when the price of pellets decreased in 2004 from 130\$/t to 65\$/t.

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