Recycling of manganese secondary raw material via cold-bond pelletizing process

Y. M. Z. Ahmed, F. M. Mohamed

Large quantities of fines were produced during the shipping, transportation, handling and storage of manganese ore sinter imported from different countries to Sinai Company for ferromanganese production. These fines are generally considered as valuable secondary raw materials. Hence, they have a potential to be recycled back to the submerged arc furnace after having been agglomerated. For agglomerates to be considered as feed materials for submerged arc furnace they must have sufficient room temperature strength. Cold-bonded pelletization process offers an economically attractive and environmentally viable method for achieving this. Ordinary Portland cement was used in this investigation for the purpose of producing a suitable coldbonded pellet from such fines. In this investigation, the effect of adding different percentages of Portland cement on the mechanical properties of both green and pellet dried at room temperature for 1, 3, 7, 14, and 28 days of normal curing were studied.
The results revealed that, although the compressive strength of green pellets improved with the increase of the amount of cement added, retardation in pellet drop strength was reported. Whereas, the increase in both the cement content and time of drying leads to increase in the mechanical properties of pellets normally cured at room temperature. Pellets obtained with the addition of 9% cement shows reasonable mechanical properties to be charged in the submerged arc furnace. Ferromanganese alloy having a standard range composition was produced in a laboratory submerged arc furnace using such pellets.

Keywords: pelletization, manganese ore, recycling, mechanical properties, cold-bond pellet

INTRODUCTION

Due to the low-grade manganese ores in Egypt, Sinai Company for ferromanganese production imports large quantities of high-grade manganese ore sinter from different countries. During the shipping, transportation, handling and storage of such sinter, a large amount of manganese ore sinter fines are produced. The amounts of these fines increased annually with the increasing demands for ferromanganese alloy. These fines could be considered as valuable secondary raw materials according to its high
manganese to iron content (~7:1), low impurities and stable chemical composition. In the mean time making use of such "waste" will solve a big environmental hazard problem to the company due to accumulation of huge amounts of these fines by time.
Due to the fineness of such secondary raw material, the pelletization process could be considered as one of the most suitable processes that deal with it. Two fundamentally different directions of pelletizing are known: high temperature method (agglomeration and production of fired pellets) and cold-bond method i.e. without firing. Generally agglomeration and firing of pellets are not cost effective (capital and energyintensive) and are extremely environmentally hazardous, since they are characterized not only by a large amount of ordinary harmful emissions (carbon monoxide, nitrogen oxide, dust ...etc) but also by super toxic dioxins and furans [1]. Cold-bond pelletizing methods recently gained some popularity. These are used when utilizing metallurgical wastes and pelleting iron, chromium and manganese materials and non-ferrous metallurgical mixtures [2]. They are characterized by low capital and current expenditures, are energy saving and environmentally safe.

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Several investigations concerning the cold bond pelletizing process had been introduced into industrial practice [2-6]. Most of these applications were interested in agglomeration of inplant fines with some waste materials like flue dust, fly ash, sludge, and other waste materials from iron and steel industry.
The aim of the present investigation is to produce suitable cold-bonded pellets from manganese fines using ordinary Portland cement as a binder. The effect of addition of different percentages of cement on the mechanical properties of both green pellets and pellets cured at room temperature for different periods of time will be studied. In addition, to confirm the viability of producing ferromanganese alloy from such pellets, suitable pellets from the mechanical properties point of view were subjected to smelting in a submerged arc furnace. Characterization of the produced alloy will be investigated.

MATERIALS AND EXPERIMENT

Materials

Manganese ore sinter fines were provided by Sinai Manganese Co., whereas Portland Cement Company of Egypt supplied the Portland cement used in this investigation.
The chemical composition of both raw materials is shown in Table. 1. The received manganese ore sinter fines were subjected to a further grinding process in a laboratory ball mill for grinding the +2 mm oversize fraction. The particle size distribution of the ground product and Portland cement were shown in table 2.

Experimental and Procedures

The pellets were prepared in a disc pelletizer of diameter 40 cm, collar height 10 cm, angle of inclination 55° and disc rotating speed 17 rpm. Batches of manganese fines (500 gm of each) were thoroughly mixed with different cement percentages (with respect to dry weight of feed charge). The raw

Components	Chemical composition, %.	
	Manganese secondary raw	Cement
Mn	42.00	--
MnO_2	1.03	--
MnO	65.10	--
SiO_2	17.10	22
CaO	1.00	63
Al_2O_3	6.00	7.5
MgO	0.25	3
Fe_2O_3	5.72	3.75
K_2O	0.30	--
P	0.09	--

Table 1 – Chemical composition of raw materials.

Tabella 1 – Composizione chimica delle materie prime.

Size range, mm.	Wt., (%)	
	Manganese secondary raw material	Portland cement
+2	0	
-2 + 1.6	0.78	
-1.6 + 1.00	2.8	
-1.00+ 0.5	3.7	
-0.5 +0.315	7.7	
-0.315 +0.125	43.3	
-0.125 +0.09	18.92	0
-0.09 +0.074	10.00	10.32
-0.074 +0.063	9.82	55.67
-0.063	2.98	34.01

Table 2 – Particle size distribution of the raw materials.

Tabella 2 – Dimensioni delle particelle delle materie prime.

mix sample was then fed to the pelletizer. The predetermined water amount percentage (with respect to dry weight of the raw mix) was then sprayed onto the rolling bed of the material in the pelletizer. The green pellet in the size range 10 – 14 mm diameter were screened out and used in the present study.
The average compressive strength of pellets was measured by compressing at least 10 green or dried pellets sample (10-14 mm) between flat parallel steel plates up to their breakage. The mean value of the tested pellets gave their compressive strength [7].
The dropping damage resistance indicates how often green or dried pellets can be dropped from a height of 30 cm before they show perceptible cracks or crumble and it measure the ability of wet pellets to remain intact during handling [C]. Ten green or dried pellets were individually dropped onto a steel plate until their breakage. The mean value of the tested pellets gave their dropping damage resistance [7].
The produced green pellets were subjected to drying by curing at room temperatures for different periods of times (1, 3, 7, 14, and 28). After each period of curing, a determination of the mechanical properties of cured pellets was carried out.
The pellets that showed suitable mechanical properties to be charged in a submerged arc furnace were, then, subjected to the smelting process. The smelting experiments for ferromanganese alloy production were produced in a 100 KVA laboratory submerged electric arc furnace. Electric power was supplied to the furnace through AC stepwise. Transformer, with primary electric power of 35 Volt and 380 Amperes, through 35-40 mm diameter of graphite electrodes, the electrodes can be moved up and down by a normal device. The inside dimensions of the furnace with tapping hole at the bottom, were 230 mm diameters and 200 mm depth. The furnace wall and bottom were rammed with magnesite. The nominal capacity of the furnace is 1-5 Kg ore. The furnace roof is furniture with water-cooled roof with three holes, two for the electrodes and one for charging. The technology of smelting is similar to the technology used in industry for production of ferro-alloys.

RESULTS AND DISCUSSION

Effect of Portland cement addition on the mechanical properties of green pellets

Figures 1 and 2, show the effect of adding different percentages of Portland cement on both the dropping damage resistance and compressive strength of green pellets. It is clear that, with increasing the percentage of cement added the dropping damage resistance of green pellets decreased. On the other hand, the situation is reversed in case of pellet compressive strength.

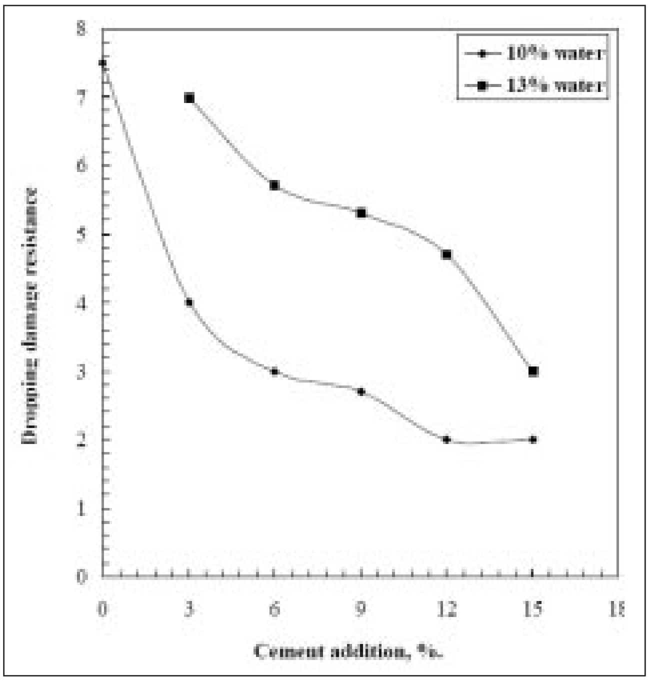

Fig. 1 – Effect of cement addition on the dropping damage resistance of green pellets.

Fig. 1 – Effetto dell'addizione di cemento sulla resistenza ai danni da caduta delle green pellets.

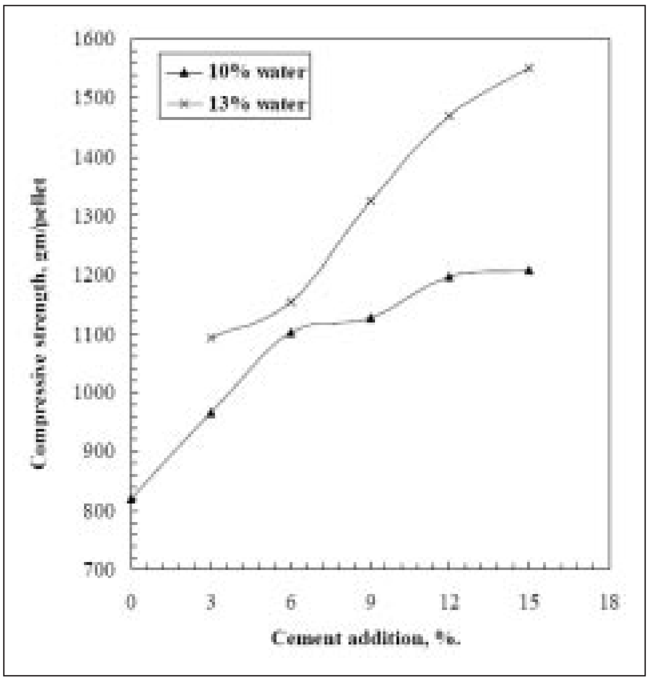

Fig. 2 – Effect of cement addition on the compressive strength of green pellets.

Fig. 2 – Effetto dell'addizione di cemento sulla resistenza alla compressione delle green pellets.

The differences in observations in case of dropping damage resistance and pellet compressive strength could be explained on the light of the mechanism of rupture that took place in each test.
In case of the dropping damage resistance test, the pellets were freely dropped from a fixed height several times over a steel plate up to their breakage. Accordingly, the strength of pellets against this drop is mainly dependent on the numbers and force of the liquid capillary “liquid bridge” formed between the feed particles during the pelletization process. These capillaries were formed as a result of the surface tension of the liquid phase that must be added for the green pellet formation [8]. This simply means that increasing the number or/and the force of these capillaries formed between the feed particles could enhance the dropping damage resistance of green pellets.
Since, when pellets having a sufficient number of liquid bridges dropped onto a steel plate, the pellet surface that touches the plate will be compacted internally to a certain degree and only a small pellet deformation could took place without pellet breakage.
After a certain numbers of drops, the pellet will not be longer having the ability for more deformation and it broke. This phenomenon could be easily observed by eye, especially in case of pellet formed with the addition of large amount of liquid, which correspondingly forms a large number of liquid capillaries between the feed particles inside the pellet. In such case, the pellet behaves like plastic since it could be dropped for large numbers and only pellets deformation without cracking or breakage took place.
With the addition of Portland cement, which has high ability to absorb water, leading to decrease in the amount of water responsible for filling every voidage between feed particles, thus decreasing the number of liquid bridges, which are responsible for developing pellet dropping damage resistance. This is confirmed from the same Figure 1, in which increasing the amount of water added from 10 to 13% at any constant amount of cement addition, leads to increase in the number of liquid bridges between particles and thus increase in the dropping damage resistance.
In case of pellet compressive strength test, the pellet brakes as a result of layer movement inside the pellet upon each other. Here not only the number and the force of the liquid bridges between the feed particles will restrict this movement but also the presence of very fine particles between the grain particles will do the same. This is because the presence of large amount of fines increases the degree of compaction, which will enhance the Van Der Waals force [9], and consequently restrict the layer movement. The increase of pellet compressive strength with increasing the amount of cement added may be due to the fact that cement has a very small particle size compared to the particle size of the manganese ore sinter fines (as shown in Table 2), leads to increase in the degree of compaction of the formed pellet and then enhance the pellet compressive strength. It seems here that there are two factors that play a role in developing the pellet compressive strength:

1 - The amount of very fine particles introduced to the feed charge
2 - The number of the liquid bridges formed during pellet formation.

The factor 1 seems to be dominant and more effective in developing the green pellet strength. Whereas, with increasing the water amount from 10 to 13% the factors 2 plays a role in enhancing the pellet compressive strength. As shown from Figure 2, that increasing the amount of water amount added from 10 to 13% at any constant amount of cement added leads to increase in the compressive strength of green pellet.

Effect of cement addition on the mechanical properties of cured pellets

Figures 3 – 6, show the effect of different amounts of cement added on the mechanical properties of pellets cured at different periods of time at room temperature. From such figures it was found that, with both increase in the cement addition and time of curing lead to increase in both dropping

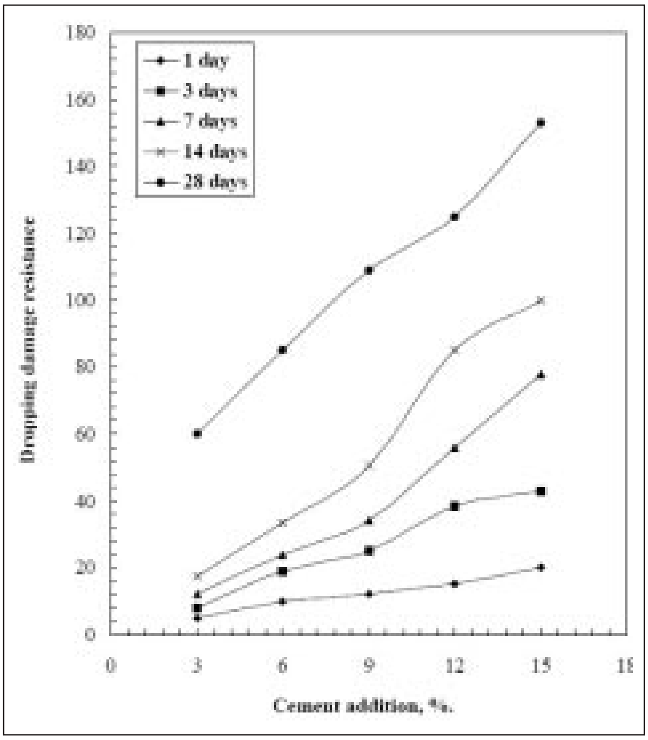

Fig. 3 – Effect of cement addition on the dropping damage resistance of pellets cured at different curing periods, (water amount = 10%).

Fig. 3 – Effetto dell’addizione di cemento sulla resistenza ai danni da caduta dei pellets con diversi periodi di stagionatura/ invecchiamento (percentuale di acqua = 10%).

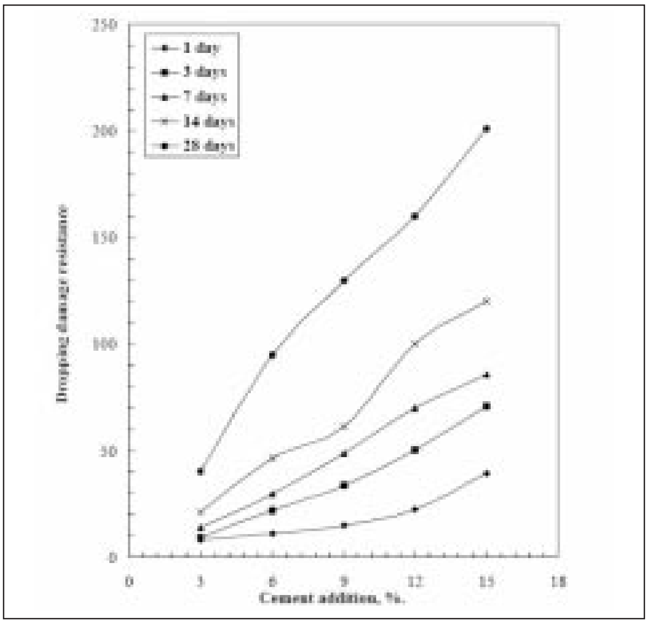

Fig. 4 – Effect of cement addition on the dropping damage resistance of pellets cured at different curing periods, (water amount = 13%).

Fig. 4 – Effetto dell’addizione di cemento sulla resistenza ai danni da caduta dei pellets con diversi periodi di stagionatura/ invecchiamento (percentuale di acqua = 13%).

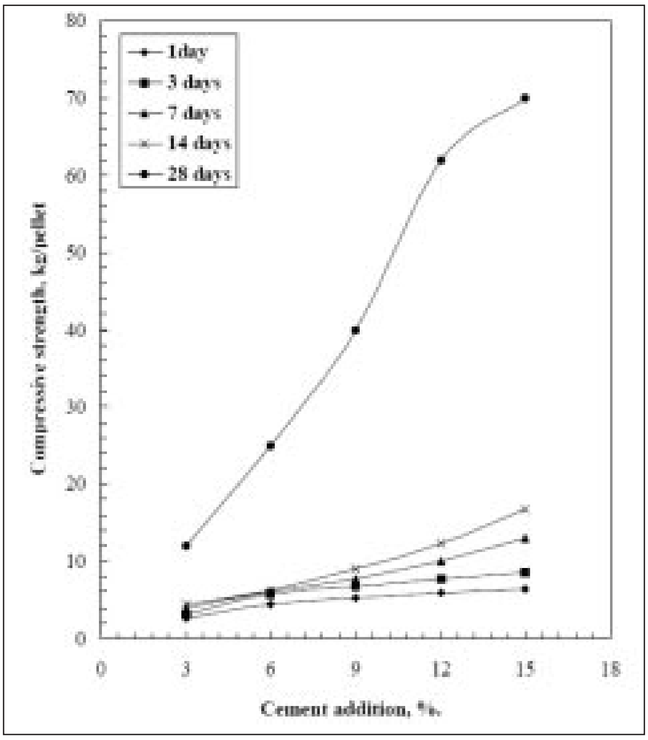

Fig. 5 – Effect of cement addition on the compressive strength of pellets cured at different curing periods, (water amount = 10%).

Fig. 5 – Effetto dell'addizione di cemento sulla resistenza alla compressione dei pellets con diversi periodi di stagionatura/ invecchiamento (percentuale di acqua = 10%).

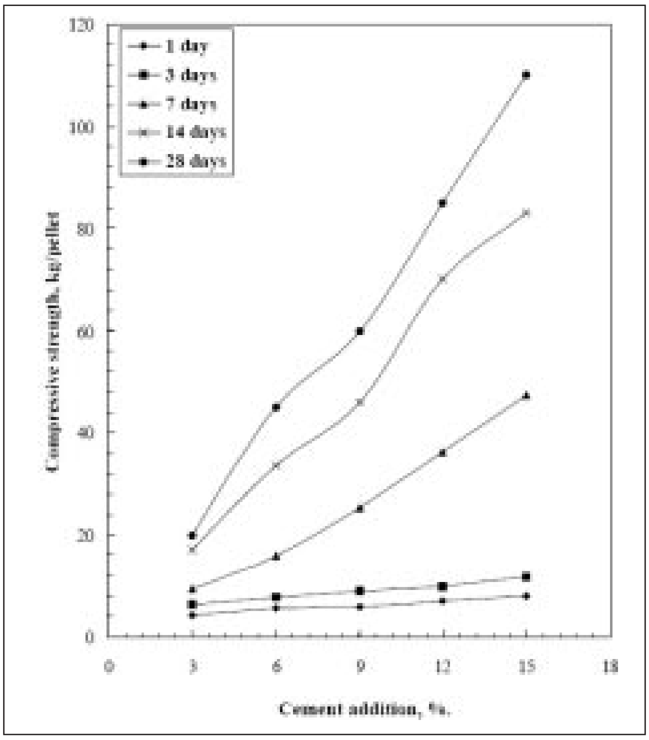

Fig. 6 – Effect of cement addition on the compressive strength of pellets cured at different curing periods, (water amount = 13%).

Fig. 6 – Effetto dell'addizione di cemento sulla resistenza alla compressione dei pellets con diversi periodi di stagionatura/ invecchiamento (percentuale di acqua = 13%).

damage resistance and compressive strength of cured pellet. Also it was clear that increasing the amount of water added from 10 to 13% leads to a remarkable increase in both the dropping damage resistance and compressive strength of cured pellets.

At any constant period of curing and at the same amount of water added, the increase of both dropping damage resistance and compressive strength of cured pellet with increasing the amount of cement added may be due to the following reasons:

1 - The main components of Portland cement are alit (tricalcium silicate) and balite (basically, dicalcium silicate). On hydration they form a gluing agent, dicalcium silicate hydrate [10], which is responsible of binding the different particles together [9]. With increasing the amount of cement added the probabilities of forming more gluing agent inside the pellets increases, which improve the mechanical properties of the cured pellets.

2 - Portland cement can be designated as an insoluble binder, which probably remains uniformly, distributed throughout a dry pellet. It imparts strength by reducing the voidage and by virtue of its extremely fine particle size, which can be expected to increase the effectiveness of the Van Der Waals forces substantially [8]. With increasing the amount of cement added the voidage reduction increases and further enhancement in the Van Der Waals forces between particles happens, which leads to a corresponding increase in the mechanical properties of cured pellets.

3 - The increase of Portland cement addition increases the degree of fineness of the whole raw mix, which increases the mechanical properties of the pellet as a result of increasing the degree of compaction and number of contact points that imparts strength to the pellet [11].

Also it was noticed that, at any constant amount of cement and water addition, the increase of the curing time leads to increase in both the dropping damage resistance and compressive strength of the cured pellets. This may be due to the continuous dissolution of calcium silicate with the increase in curing time resulting in precipitating of more gluing agent dicalcium silicate [10]. It may also be due to the tendency for better crystallization of the hydrated products responsible for strength enhancement [12].

It could be noticed from the same figures that at any constant amount of cement addition and at any constant curing time, the increase of water addition from 10 to 13% leads to increase in both the dropping damage resistance and compressive pellets of cured pellets. This may be due to the fact that for developing a reasonable strength for cold bond agglomerate using Portland cement it is necessary to add a suitable and sufficient amount of water. This necessity comes from the fact that, the phase responsible for developing the strength in such agglomerate, calcium silicate hydrate, (CSH) could be obtained from the reaction between calcium silicate "which is already present in Portland cement" and water. Insufficient amount of water added during pelletization of the feed charge results in formation of a lesser amount of this gluing agent inside the formed pellets. Whereas, with increasing the amount of water added leads to increasing the probability for the formation of large amount of such gluing agent inside the formed pellets. Consequently, better crystallization of such phase during different periods of curing is also responsible for strength enhancement.

Production of ferromanganese alloy

From the previous investigation on the effect of Portland cement addition on the mechanical properties of cured pellets, it was noticed that, the pellet compressive strength increased with increasing the cement addition. It could reach about 116 kg/pellet for pellet formed with the addition of 15% cement and 13% water and cured for 28 day at room temperature. While, the increase in the cement content helps by increasing the pellet strength, it adversely affects the production cost of the pellets. To some extent, increased addition

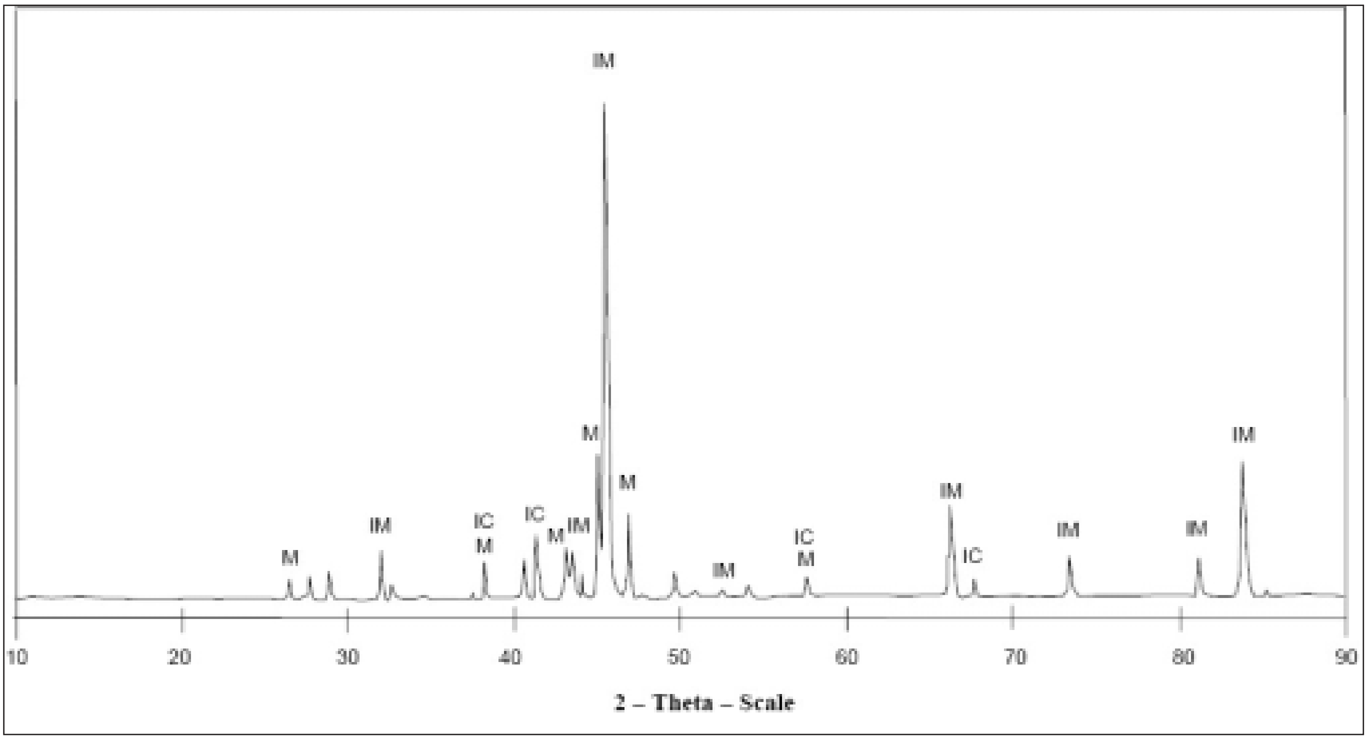

Fig. 7 – XRD of ferromanganese alloy produced from the smelting of manganese ore sinter fines cold bonded with 9% cement addition.

Fig. 7 – XRD di una lega di ferromanganese prodotta mediante smelting di manganese ore sinter fines legate a freddo con aggiunta di cemento al 9%.

may also affect the submerged arc furnace operation.

The lime part of the cement may be compensated by the lower addition of limestone that must be added during the alloy production, but the silica part has to be end up as molten slag. This will contribute in increasing of the energy requirements due to more generation of molten slag. For the previous reasons, it is important to keep the cement content as low as possible to avoid increasing in the energy requirement for smelting of these pellets. In the same time, it is important that these pellets must have compressive strength that meets the requirement of the submerged arc furnace (60 kg/pellet or more) [13]. Accordingly pellets produced at 9% cement and 13% water and cured for 28 days at room temperature, could fulfill the compressive strength requirement and also it is the minimum amount of cement added for obtaining such strength. About 2 kg of pellets under the condition of; amount of cement = 9%, water amount = 13%, and curing time = 28 day at room temperature, were prepared for subsequent smelting in the laboratory submerge arc furnace. The produced ferromanganese alloy was then characterized, as follows.

Table 3, shows the chemical composition of the produced ferromanganese alloy.

From this Table it could be noticed that the ferromanganese alloy produced from the smelting of these pellets has a chemical composition within the standard ferromanganese alloy composition. Fig. 7 shows the XRD of the produced ferromanganese alloy. It could be noticed that the main components of this alloy are iron manganese FeMn4, manganese, and iron carbide Fe2C.

CONCLUSION

While the addition of Portland cement enhances the green pellet compressive strength it retards the green dropping damage resistance. This is due to the difference in the mechanism of pellet rupture that took place in each test. Increasing amount of water added improves to a large extent the mechanical properties of green pellets as a result of increasing the number of liquid bridges inside the pellets. The amount of cement, amount of water added, as well as the curing time of pellets at room temperatures play very important roles in the mechanical properties of the produced pellets. Pellets produced with 9% cement and 13% water and cured at room temperature for 28 days show reasonable properties. The ferromanganese alloy produced from the smelting of these pellets has a chemical composition within the range of the standard alloy.

Components	Percentage, %	
	Standard alloy	For alloy produced from pellets containing 9% Portland cement
Mn	75-79	76.73
Fe	16-12	14.23
P	< 0.2	0.17
Si	< 1.2	1.01
C	< 7.5	6.52

Table 3 – The chemical composition of ferromanganese alloys.

Tabella 3 – Composizione chimica delle leghe di ferromanganese.

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A B S T R A C T

RECICLO DI MATERIALE SECONDARIO DI MANGANESE MEDIANTE PROCESSO DI COLD-BOND PELLETIZING

Parole chiave:
processi, riciclo

Durante il trasporto, la movimentazione e lo stoccaggio dei minerali di manganese sinterizzati, importati da diversi paesi da parte della Sinai Company per la produzione di ferromanganese, si sono prodotte grandi quantità di polveri.
Queste polveri generalmente vengono considerate come importanti materie prime secondarie e sono potenzialmente impiegabili come materiale di riciclo nel forno ad arco sommerso, dopo un processo di agglomerazione.
Per poter essere utilizzati come materiali per alimentare il forno ad arco, gli agglomerati devono possedere una sufficiente resistenza meccanica alla temperatura ambiente. Il processo di pellettizzazione a freddo consente di ottenere le caratteristiche necessarie con un metodo interessante sia dal punto di vista economico che ecologico. In questa ricerca è stato utilizzato, insieme alle polveri, del normale cemento Portland per produrre pellet legate a freddo adatte all' impiego, e sono stati studiati gli effetti dell'aggiunta di diverse percentuali di cemento Portland sulle proprietà meccaniche sia di pellet a verde che di pellet essiccate, con normale invecchiamento a temperatura ambiente, per 1, 3, 7, 14 e 28 giorni. I risultati hanno evidenziato che, nelle pellet a verde, sebbene la resistenza alla compressione sia risultata migliorata aumentando la quantità di cemento aggiunta, si è osservata un peggioramento nella loro resistenza alla caduta. Invece, aumentando sia contenuto di cemento che il periodo di essiccamento, si è ottenuto un miglioramento delle proprietà meccaniche delle pellet invecchiate a temperatura ambiente. Le pellet, ottenute mediante l'aggiunta del 9% di cemento, hanno mostrato proprietà meccaniche appropriate per l'utilizzo nel forno ad arco sommerso. Utilizzando tali pellet è stata quindi prodotta in laboratorio una lega di ferromanganese con composizione standard per l'impiego in un forno ad arco.