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Electrolytic Preparation of Iron Powder with Particle Size Less than 106 µm

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Abstract

Avery large numbers of articles are made by powder metallurgical methods using electrolytically reduced metal powders. Iron powder is one of these powders which play an important role in this field. Its preparation by electrolytic method is economic in comparison with the traditional methods (Atomization and carbonyl processes).

An electrochemical cell consisting of two electrodes (stainless steel cathode and iron anode, 99.9%) was used to study the electrolytic preparation of iron powder with particle size less than 106µm directly as powdery form. Ferrous sulphate electrolyte was used containing sodium chloride as a stabilizing agent. The produced powder was thoroughly washed with an acidified distilled water and absolute ethanol, then dried under an inert atmosphere at 80oC, and classified by screening. Samples of prepared powder were taken to determine their purity by atomic absorption. The effects of current density, metal ion concentration, sodium chloride concentration, PH, and electrolysis time on the weight percent of iron powder less than (106µm), yield and current efficiency were studied.

It was found that an iron powder with particle size less than 106µm can be prepared at a weight percent of iron powder less than 106µm (89.7%) and current efficiency of 71% using cathodic current density of 0.1 A/cm^2 and electrolysis time equal to 1 hr. The prepared powder having an apparent density of (3.24 gm/cm^3 and real density of 7.39 gm/cm^3 with specific surface area of 238 X 103 cm^2/gm. Its average particle size was 75 µm and its purity was 99.14%.

Keywords: iron powder, electrolytic iron, electrodeposition of iron, electrolytic preparation.

Introduction

Iron powder plays an important role in the industry, it accounts for 80% by weight of all metal powders produced annually [1].It is used extensively in the manufacturing of various automobile sintered parts and electromagnetic materials such as: the dust core, oxygen absorber and body warmer by using powder metallurgy (P/M) technique which is the most diverse manufacturing approach among the various metal working technologies due to its ability to fabricate high quality and complex parts to close to tolerances in an economical manner. Iron powder is also used as a carrier for toner in electrostatic copying machines and a chemical raw material to recover metals of value in the process effluent [2].

Iron powder are manufactured through several different methods of production with each yielding a product that has distinct physical properties, four principal methods by which iron powders are commercially produced: Atomization, Chemical reduction, Thermal reduction and electrolytic method. Atomization is the oldest method and still dominant for producing iron powders although it requires high energy. The chemical method has also been used where selected ore is crushed ,mixed with carbon and passed through a continuous furnace where reaction takes place leaving a cake of spongy iron which is then further treated by crushing .since no refining operation is involved ,the purity of the product depends on that of the raw materials. Carbonyl process was originally developed as a means of refining of iron where crude metal being caused selectivity to react with carbon monoxide under pressure to form the carbonyl which is a gaseous at the reaction temperature and decomposed on raising the temperature and lowering the pressure to obtain pure iron powder and carbon monoxide [3].

The electrolytic method is the most economical method for producing iron powder; moreover the iron powder obtained is the highest quality. The electrolytic powder consists of particles whose dimensions and form (dendritic shape) are more suitable for pressing. The major advantage of electrolytic method over the other methods lies in the possibility of conducting the process under conditions such that powders of a wide range of volumetric mass are obtained (0.4-4.0 gm/cm^3).

Nevertheless the preparation of iron powder by electrolysis is carried out on an industrial scale and the production continuous to increase; therefore the electrolytic method deserves a special attention. The techniques for electrodepositing of iron powder have advanced in two directions: electrodeposition of fragile deposits, which by grinding yield powders and electrodeposition of powder directly.

Several parameters influences on the characteristic and structure of iron powder produced as well as the yield and current efficiency which play an important role on the economy of the process .These are :metal ion concentration ,current density ,agitation ,temperature, conductivity of electrolyte and added colloids to solution. current density and metal ion concentration are more pronounced on the yield and current efficiency [4].

Electrodeposition of iron powder dates back to 1846 when Bottger used a bath of ferrous sulphate and ammonium chloride [5] .Siemens in 1889 proposed a general process in which sulfide-iron minerals were leached with ferric chloride or sulfate [6]. The first serious attempt to produce electrolytic iron in quantities was in 1904, when the metal was deposited at a current density of 0.006-0.01 A/cm^2 at 30°C and an average emf of 1 volt [7]. In 1914 an electrolytic iron plant was installed at Grenoble, France, in which a hot natural solution of ferrous chloride was employed as an electrolyte to which iron oxide was added as a depolarizer, with cast iron anodes [8].Clarence proposed an electrolyte for the electrodepositing of iron for powder metallurgy purposes consisting essentially of an aqueous solvent and solute of ferrous chloride, ammonium sulfate and ferrous sulfate being in the ratio 1:7:9 [9].

Zhelibol in 1973 prepared fine powder by using concentrated solutions under the conditions of a two-layer electrolytic bath [10]. Samal discovered an improved process for producing iron powder wherein at least 70% weight fraction of powder is less than 44 microns by using an aqueous electrolytic bath at a ferrous ion concentration of 36-40 gm/l and maintaining the pH at the range of 5.6-6.0 and temperature of 38-49°C [11].

Chul studied the effect of some additives such as oxalic and citric acid on the cathodic polarization and current efficiency; he deduced that such additives produced fine powders with no dendrites [12].

Carlos studied the galvanostatic iron electrodeposition on nickel substrate and obtained fragile layers at current density of 0.04 A/cm^2 which can be transformed into pure iron powder [13].

The aim of the present research is to prepare an electrolytic iron powder directly in powdery form rather than compact deposits which must be milled as known in the previous works.

Experimental Work

The iron powder electrodeposition was carried out at constant current operation during the electrolysis (galvanostatically) using a 3.5-liter capacity electrolytic cell (made of Perspex) having provision for electrode adjustment in all required directions as shown in Fig. 1.

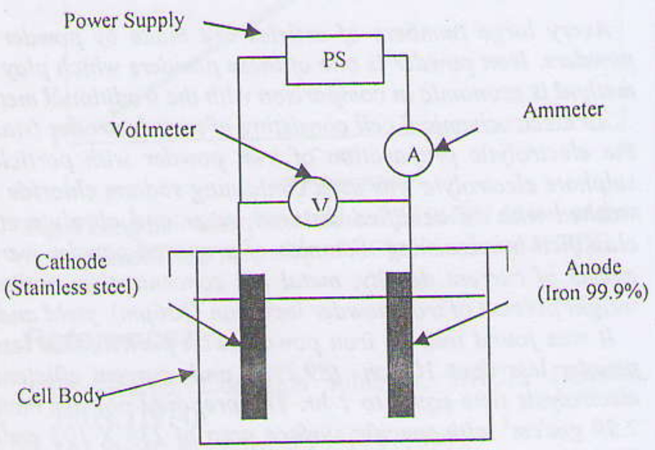

Fig. 1 Electrolytic cell

The dimensions of the cell were 18x32x6 cm having a top coversheet. the cell consisting of two electrodes: cathode made of stainless steel plate of 30cm length and 16cm width and anode made of iron plate of 30cm length and 16cm width having a purity not less than 99.9%. An enter electrode distance of 3 cm was maintained .The effective surface area of cathode (immersed area) suitable for applying the limited current density was determined by moving vertically the cathode up or down the level of the electrolyte The two electrodes were first subjected to mechanical treatment with first rough and fine emery paper, kept in dichloroethane in order to remove any grease from the electrode surface, shaken in distilled water for a few minutes and wiped with drying paper before being placed in the cell. A power supply

(20ampers, 30 volt) was used to driven the circuit, total current of 10 amperes was applied for each run and the electrolysis was proceeded at room temperature.

All the reagents used for preparing the electrolyte were of analytically grade (Merck) and did not undergo further purification .distilled and deionized water was used in preparing the solutions. A 2.5-liter electrolyte was prepared for each run by dissolving ferrous sulphate and sodium chloride in an acidified distilled water. The amount of ferrous ion in the electrolyte at the starting and during the electrolysis was determined by using atomic absorption technique. the PH of electrolyte was detected online .At the end of each run , iron powder was scraped out the cathode , washed with distilled water (Luke-warm and acidified , pH=2) and absolute ethanol , dried under nitrogen atmosphere at 80°C, screened using 106 µm sieve and weighted the two cuts (upper and lower than 106µm). Samples of the prepared powder were taken to determine their purity by atomic absorption. The cathode in turn was rinsed in dilute HCl and made ready for subsequent use. Factorial experimental design was used to study the effect of the main parameters on the percent of powder having particle size less than 106µm, current efficiency and yield.

Results and Discussion

The effects of the main parameters were studied in order to determine the preferred conditions for obtaining iron powder directly in powdery form at higher percent of particle size less than 106µm with a suitable current efficiency.

Current density

Fig. 2-4 shows the effect of current density on the percent of iron powder less than 106µm, current efficiency and yield respectively.

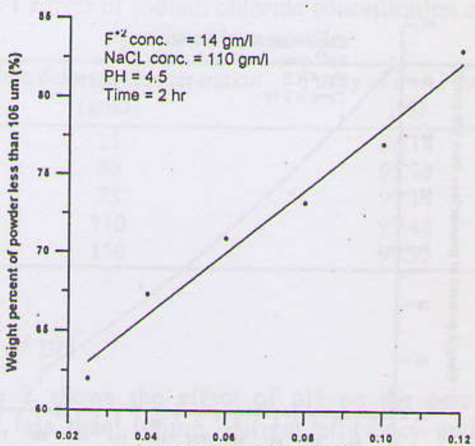

Fig. 2 Effect of current density on weight percent of powder less than 106 µm

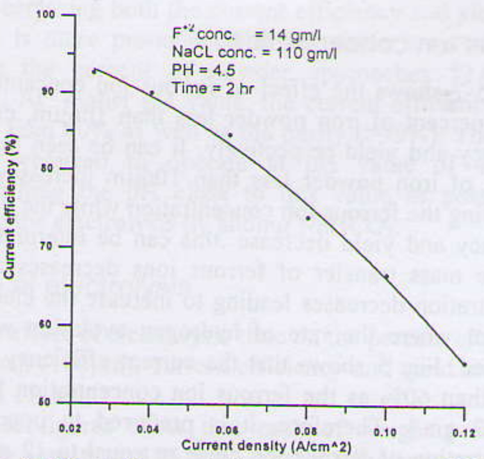

Fig. 3 Effect of current density on current efficiency

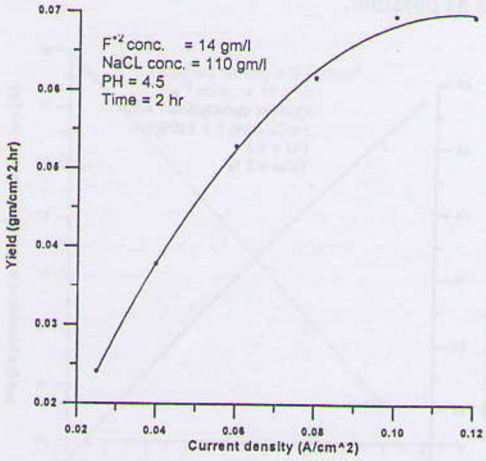

Fig. 4 Effect of current density on yield

It can be seen that the percent of iron powder and yield increase with increasing the current density while the current efficiency decreases. This is because of the increasing in the rate of hydrogen evolution as current density increases leading to increase the penetration and distribution of hydrogen bubbles through the bed of iron powder formed on the cathode surface which make the particles of iron finer. It is to be noted that current efficiency drops down (60%) as the current density reaches 0.12 A/cm^2 .From practical view point, it is not recommended that the current efficiency reduces lower than 60% because of a high electrical energy will be lost and to avoid excessive heating of the electrolyte and formation of dendritic-tree growths on the cathode and to maintain a useful electrolytic deposition rate. In addition, the temperature of the electrolyte reached to 55°C at current density of 0.12 A/cm^2 as observed in the experiments. the temperature increasing led to increasing the ferrous ion concentration in the electrolyte as the current density rose higher than 0.1A/cm^2, also iron hydroxide was precipitated which caused some problems in the electrolyte. These results in accordance with that obtained by Samal [11].

Ferrous ion concentration

Fig. 5-7 shows the effect of ferrous ion concentration on the percent of iron powder less than 106μm, current efficiency and yield respectively. It can be seen that the percent of iron powder less than 106μm increases with decreasing the ferrous ion concentration while the current efficiency and yield decrease .this can be interpreted as that the mass transfer of ferrous ions decreases as the concentration decreases leading to increase the electrode potential where the rate of hydrogen evolution will be increased. Fig. 5 shows that the current efficiency drops lower than 60% as the ferrous ion concentration lowers than 12 gm/l. Therefore, it is preferred to operate at concentration of ferrous ion close or equal to 12 gm/l to insure the current efficiency being higher than 60% and maintaining the percent of iron powder less than 106μm as high as possible.

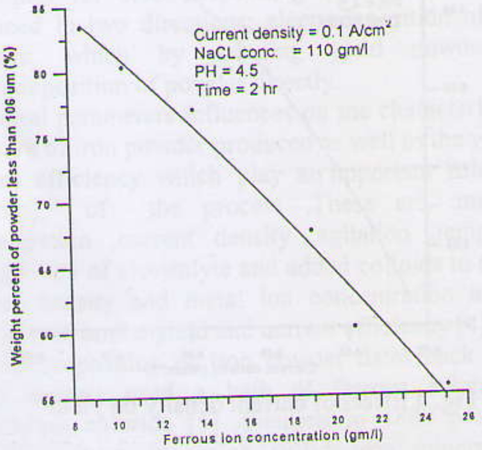

Fig. 5 Effect of ferrous ion concentration on the weight percent of powder less than 106 μm

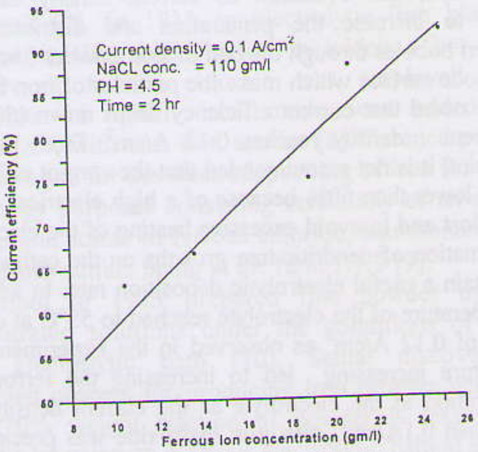

Fig. 6 Effect of ferrous ion concentration on the current efficiency

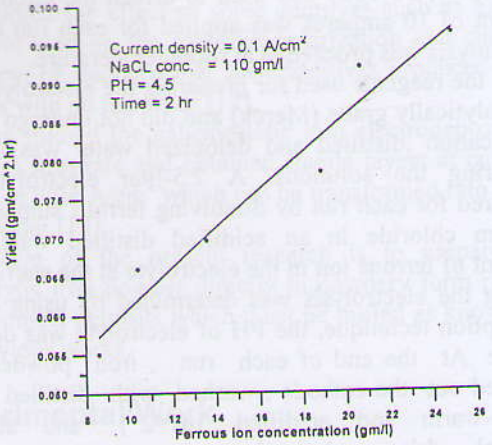

Fig. 7 Effect of ferrous ion concentration on the yield

Sodium chloride concentration

Fig. 8-10 shows the effect of sodium chloride concentration on the percent of iron powder less than 106μm, current efficiency and yield respectively. It is observed that any increasing in sodium chloride concentration leads to decreasing the percent of iron powder less than 106μm and increasing the current efficiency and yield .the effect is not critical as those in the current density and ferrous ion concentration, however, sodium chloride stabilizes the electrolyte and increases its conductance. It also affects the form of deposit, which is granulometrically more uniform.

The main effect of sodium chloride concentration is on the purity of iron powder obtained as shown in Table 1 where the purity of powder decreases lower than 86.4% as concentration approaches 25gm/l while it is higher than 99% at concentration equal or higher than 75gm/l.

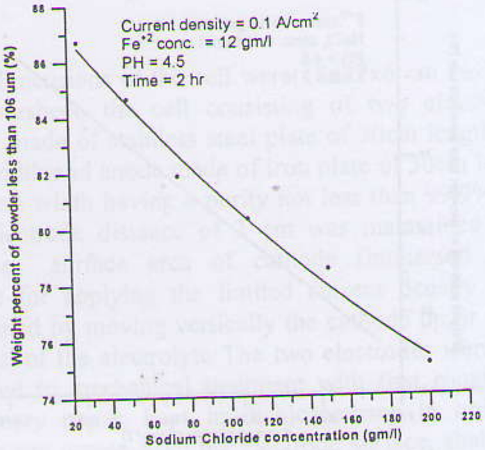

Fig. 8 Effect of sodium chloride concentration on the weight percent of powder less than 106 μm

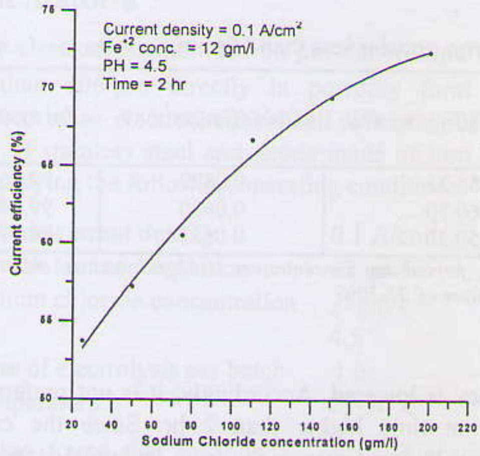

Fig. 9 Effect of sodium chloride concentration on the current efficiency

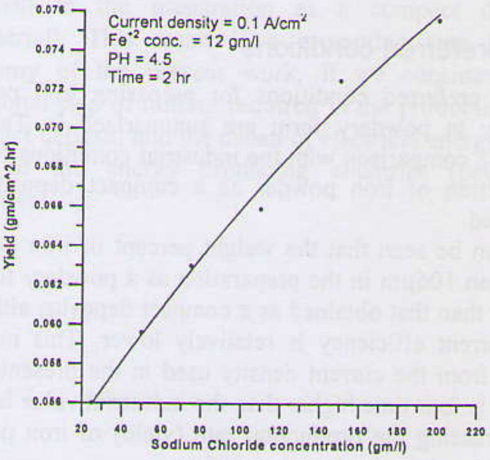

Fig. 10 Effect of sodium chloride concentration on the yield

Table 1 Effect of sodium chloride concentration on the purity of iron powder

Sodium chloride Concentration (gm/l)	Purity of iron Powder (%)
25	86.14
50	95.78
75	99.14
110	99.48
150	99.52

Effect of pH

Table 2 shows the effect of pH on the percent of powder less than 106µm, current efficiency and yield respectively at three values of pH.

It is cleared that any increasing in pH value leads to increasing the percent of iron powder less than 106µm and decreasing both the current efficiency and yield. The effect is more pronounced at pH value lower than 4.5 where the percent of powder approaches 52.65% at pH=2. At higher pH value, the current efficiency drops lower than 60% as well as the purity (>99%). Therefore, it is preferred to operate at pH value of 4.5 and maintaining the pH close to this value as possible as during the electrolysis by adding $NaHCO_3$.

Time of electrolysis

The effect of electrolysis time on the percent of powder less than (106µm), current efficiency and yield are given in Fig. 11-13.

These figures show that each of weight percent of powder less than 106 µm, current efficiency and yield decrease with increasing the time. This is because of the increasing in the effective area of the cathode as time

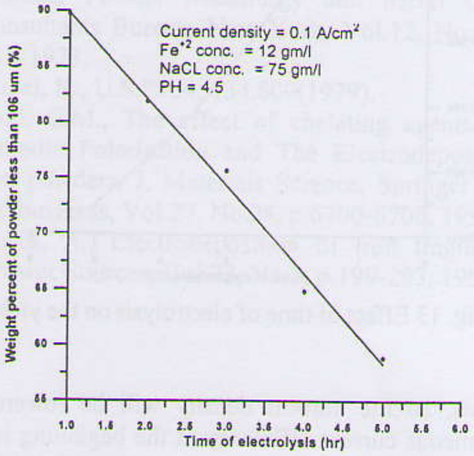

Fig. 11 Effect of time of electrolysis on the weight percent of powder less than 106 µm

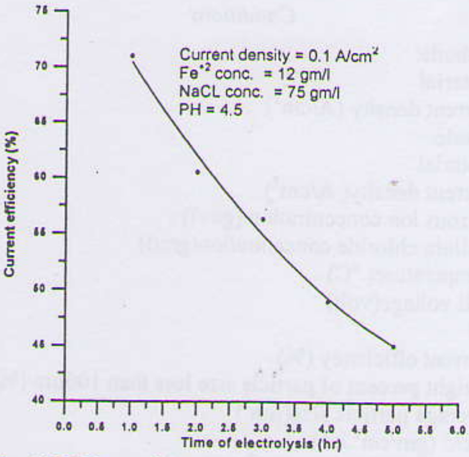

Fig. 12 Effect of time of electrolysis on the current efficiency

Table 2 Effect of PH on the percent of iron powder less than 106μm

pH	*Percent of iron powder (%)*		*Current efficiency (%)*	*Yield (Gm/cm².hr.)*	*Purity (%)*
	Higher than 106μm	*Less than 106μm*			
2.0	47.35	52.65	86.35	0.0899	99.56
4.5	18.13	81.87	60.50	0.0630	99.14
6.0	10.20	89.80	50.36	0.0522	96.37

current efficiency and yield were at current density of 0.1 A/cm², ferrous ion concentration is 12gm/l, sodium chloride concentration is 75g/l, time of electrolysis per batch is 1 hr and temperature of 25-30°C

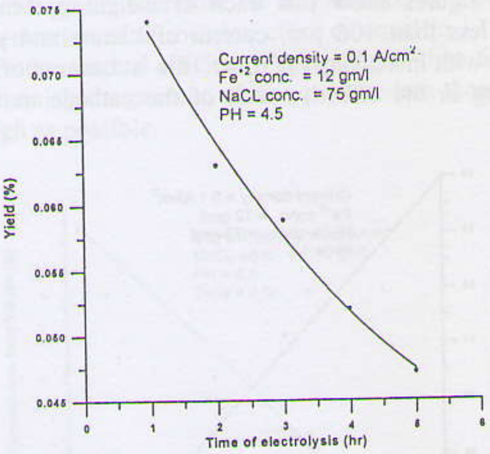

Fig. 13 Effect of time of electrolysis on the yield

increases, so the current density will be lowered .the instantaneous current efficiency at the beginning is lower than that at the end, however, the accumulative current efficiency is lowered. Accordingly, it is not preferred to operate at time higher than 2 hr. Since the current efficiency lowered than 60%, from technical standpoint, the powder must be removed periodically after 1 hr to insure high percent of powder less than 106μm at reasonable current efficiency.

The preferred conditions

The preferred conditions for preparing iron powder directly in powdery form are summarized in Table 3 where a comparison with the industrial conditions for the production of iron powder as a compact deposits are included.

It can be seen that the weight percent of iron powder less than 106μm in the preparation as a powdery form is higher than that obtained as a compact deposits, although the current efficiency is relatively lower. This may be result from the current density used in the present work which is four time higher than the industrial value leading to increasing the production rate (yield) of iron powder having particle size less than 106μm.

Table 3 Comparison between the present work and industrial conditions

Conditions	*present work (powdery deposits)*	*Industrial [2] (compact deposits)*
Cathode:		
Material	Stainless steel	Iron (99.9%)
Current density (A/cm²)	0.1	0.027
Anode:		
Material	Iron (99.9%)	Iron (99.9%)
Current density(A/cm²)	0.1	0.027
Ferrous ion concentration (gm/l)	12	50
Sodium chloride concentration(gm/l)	75	---
Temperature(°C)	25-30	50
Cell voltage(volt)	3.2	2.5
pH	4.5	4.5
Current efficiency (%)	71	90
Weight percent of particle size less than 106μm (%)	89.7	78
Average particle size(μm)	75	63
Yield (gm/cm².hr.)	0.074	0.0233
Specific surface area(cm²/gm)	238 X 10³	452 X 10³
Apparent density(gm/cm³)	3.24	2.56

Conclusions

The electrodeposition of iron powder with particle size less than 106 µm directly in powdery form can be achieved by an electrochemical cell consisting of cathode made of stainless steel and anode made of iron (99.9%) and applying the following operating conditions:

• cathode current density	0.1 A/cm^2
• Ferrous ion concentration	12 gm/l
• Sodium chloride concentration	75gm/l
• pH	4.5
• Time of electrolysis per batch	1 hr
• Temperature	25-30°C

It was found that the powder obtained according to above conditions has a weight percent of particle size less than 106µm close to 90% and an average particle size 75 µm with a production rate three time higher than obtained in the preparation as a compact deposits (industrial). This result is a promoting step for the economy of the present work, if we considered the additional step of milling required in the production as a compact deposit, and the cheap of electrical energy in the case of the energy producing countries (petroleum countries).

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