PRODUCTION AND PROSPECTS FOR APPLICATION OF FERRIC OXIDES TO ALKALINE ACCUMULATORS BASED ON FERRIC-BEARING PRODUCTS OF WIRE PRODUCTS INDUSTRIES

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It is common knowledge that one of the main components in manufacturing a negative electrode of nickel-iron lamella accumulators is artificial ferric oxide. In UIS countries, especially in Russia, Ukraine, Kazakhstan, nickel-iron accumulators are in rather common use. They are applied with profit to mine electric locomotives, railway and floor electric transport. Their primary advantage is a long term of service (more than 1000 cycles), high reliability and unpretentiousness while using in the most severe conditions (deep discharge, current overloads, vibratory and impact loads).

When the natural sources of iron-ore raw material applied, after its concentration for making a negative electrode of nickel-iron accumulators artificial ferric oxide is used as addition. The principal role of it is to obtain the wanted specific surface area of negative electrode active material in subsequent reconditioning to provide the required electric characteristics of accumulators.

In spite of existing demand of UIS accumulator plants for this products in the early 90-s its output was actually ended. This problem was especially pressing for "Lugansk Battery" JSC ("LB" JSC), whose main product range consisted of nickel-iron accumulators.

The pilot commercial plant of a ferric (III) oxide production for accumulators with capacity of 50 t/year with the use of ferric-bearing raw material of iron wire by-product as an initial one was created in 1999 on the authors initiative to satisfy the demands of "LB" JSC.

The technology of α-ferric (III) oxide production is based on ferric vitriol aqueous solution deposition of magnetite by partial oxidation of iron ions (II) up to the iron (III) at definite pH with the subsequent washing and treatment of sediment.

From the 1999 to 2001 the product was manufactured to specification Industrial Standart 160.5009.001-73, quality "A". The essential requirements to the product were the following quality indeces:

- Iron fraction of total mass, no less than 69%,
- Content of manganese impurity (Mn/Fe ratio), no more than 0.05%,
- Content of calcium, magnesium, aluminium impurities (Ca/Fe ration, Mg/Fe ratio, Al/Fe ration), no more than 0.02%,

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Sulphate-ion impurities content (SO_4/Fe ratio) in specification Industrial Standart 160.5009.001-73 is no more than 1.45%. But for ferric electrodes made by "LB" JSC technology this requirement is not essential because while manufacturing electrode material oxidized sulphur reduces to sulphide if heat treated and becomes positive addition for it inhibits electrode passivation.

At the stage of pilot-commercial technological tests the emphasis was made on the improvement of α-ferric (III) oxide properties and new marketable product forms development. At this period more than 80 t of product were manufactured and given for testing to "LB" JSC. As a result, after the refinement of individual units and devices and technology improvement it managed to get the product with better physical and chemical composition and electro-chemical indices than before, and cheaper.

At the same time the technology was worked out in the laboratory conditions and a new marketable form of ferric oxide got; single-phase mixture of magnetite (Fe_3O_4) and γ-ferric (III) oxide (γ-Fe_2O_3) having a crystal structure with spinel lattice constant (for different prototypes) from a=8.386Å to a=8.396Å in which the percent by ferric content is higher and reaches 72%.

The joint work of obtaining electrochemical active magnetite form done together with "LB" JSC. Enabled to set up its industrial production the reafter.
The data on testing two pilot batches of magnetite obtained by "LB" JSC is cited as an example below in Table 1.

Table 1 *Chemical and electrical properties of ferric oxides*

№ part	№ 44			№71		
№ sample	1	2	3	1	2	3
Weight, g	8.53	8.49	8.51	8.49	8.52	8.49
Fe total, %	70.1			69.9		
FeO, %	12.1			11.6		
Fe_2O_3	86.5			86.85		
SO_4/Fe, %	1.96			2.25		
cycle	Lamella capacity, A·h (the requirement is no less than 1.25A·h)					
1	0.59	0.59	0.57	0.63	0.62	0.62
2	0.88	0.85	0.87	1.03	1.05	1.03
3	1.20	1.14	1.15	1.22	1.22	1.20
4	1.47	1.48	1.47	1.28	1.28	1.27
5	1.57	1.55	1.57	1.40	1.40	1.40

As distinct from a-ferric (III) oxide the obtained crystal structure has rather high specific magnetization (in the range if (50÷80) A.m^2/kg) and must offer better electrochemical characteristics when used in ferric electrode material.

Relying on bench testing and pilot commercial tests in 2002 by "ProfCom" Ltd Specifications of the Ukraine TUU 24.1-30465504-001-2002 for ferric oxides were developed, approved and validated. Below in the Table 2 given the specifications for products.

Table 2 *Physical and chemical characteristics of ferric oxides*

Index denomination	Norm	
	ferric oxide (III)	ferric oxide (II,III)
1. Ferric fraction of total mass, % no less than	69.00	70.00
2. Sulphate-ion fraction of total mass to ferric fraction of total mass ratio, SO_4/Fe, %, no more than	2.00	2.00
3.Residuel insoluble in hydrochloric acid fraction of total mass to ferric fraction of total mass ratio, %, no more than	0.29	0.29
4. Sieve analysis: fraction + 1,5 mm, %, no more	5.00	5.00
5. Calcium fraction of total mass to ferric fraction of total mass ratio, Ca/Fe, %, no more than	0.02	0.02
6. Magnesium fraction of total mass to ferric fraction of total mass ratio, Mg/Fe, %, no more than	0.02	0.02
7. Manganese fraction of total mass to ferric fraction of total mass ratio, Mn/Fe, %, no more than	0.05	0.05
8.Aluminium fraction of total mass to ferric fraction of total mass ratio, Al/Fe, %, no more than	0.02	0.02
9. Chromium fraction of total mass to ferric fraction of total mass ratio, Cr/Fe, %, no more than	0.02	0.02
10. Titanium fraction of total mass to ferric fraction of total mass ratio, Ti/Fe, %, no more than	0.02	0.02
11. Vanadium fraction of total mass to ferric fraction of total mass ratio, V/Fe, %, no more than	0.01	0.01

Besides, in pilot conditions obtained the batches of fine crystal magnetite with a particle size of 0.8 ± 1.5 micron and sulphate-ion impurity content in the ratio SO_4/Fe of less than 0.5%.

At present the customers circle of ferric oxides for accumulators has been increased. We deliver α-ferric (III) oxide to firm “Bochemie” s.r.o. for making negative active material in accordance with TUU but sulphate-ion impurity content does not exceed 1.45%.

First, the ferric oxide sample produced by “ProfCom” Ltd were tested by the company of “Bochemie” s.r.o. for the compliance with their requirements for both chemical composition and electrochemical characteristics. The data are given in Table 3.

Table 3 *The results of Fe_2O_3 analysis carried out by "ProfCom " Ltd Donetsk*

Index	Bochemie's requirement	The results of analysis	
		«Bochemie»	«ProfKom Co»
Fe	min 69.0	70.32	72.4
sulphate-ion	max 1.45	1.30	1.04
Mn	max 0.05	0.02	0.02
Al	max 0.02	0.001	0.001
Ca	max 0.02	0.000	0.014
Mg	max 0.02	0.001	0.003
Residue insoluble in HCl	max 0.29	0.085	0.0072
Residue sieve +1.0 mm	max 5.0	6.5	< 5.0

The variations in the obtained results of chemical analysis are explained by the difference of component determination techniques. The analysis with the use of "Bochemie" determination technique is performed to ferric oxide mass, one the use "ProfCom" Ltd is carried out to ferric fraction of total mass. For this fact the results of "ProfCom" Ltd had to be recalculated to ferric oxide mass. This is a difference between the results of sulphate content (it may be influenced by the use of difference technique), but the content of sulphates meets "Bochemie" s.r.o. requirements. The residue on sieve of 1 mm is a bit higher. "ProfCom" Ltd determines the residue on sieve of 1.5 mm "Bochemie" does on sieve of 1 mm.

As for electrochemical activity the negative material was made of ferric oxide and its activity was tested according to the common technique of "Bochemie" s.r.o. The obtained results of sample activity:

- Cycle No 1 – 264.8 mAh/gr;
- Cycle No 2 – 309.8 mAh/gr;
- Cycle No 3 – 310.1 mAh/gr;
- Cycle No 4 – 305.5 mAh/gr;
- Cycle No 5 – 301.4 mAh/gr.

The activity of sample agrees with the activity of materials manufactured in production quantities.

Currently the deliveries geography is extending. Pilot-commercial batches of ferric (II,III) oxide by weight of 26 ton were delivered to "Kursk Battery" JSC, according to the data of there representatives the test results are good.

So as a result of 5 years long work package (research and development, experimental, pilot- commercial work) carried out by some enterprises it managed to create the industrial product of ferric oxides necessary for manufacturing alkaline, accumulators on the basis of by-products of metal processing industry.