

## Application of high calorific mixtures in reverse batteries

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**Abstract:** Chemical sources of energy, operating effectively within a wide range of temperatures, not prone to self-discharging during a long period of storage in varying environmental conditions, featuring a very short activation time and differing in construction from the commercially available energy sources, are called reserve batteries.

Following the way of activation, there are the following battery types: water-activated, electrolyte-activated, gas-activated and heat-activated batteries. At the ambient temperature below zero, some of the types included in the first three groups require thermal activation, particularly in the initial period of operation. Thermally activated batteries supply the useful energy only when the temperature of their cells exceeds 350 °C. The activating agent for batteries is usually a high calorific mixture: Zr/BaCrO<sub>4</sub> or Fe/KClO<sub>4</sub>. It is being reported that physical and chemical properties of this mixture ingredients determine the basic operational parameters of the battery, such as activation time, amount of thermal energy being released, volume of the emitted gases, linear burning rate and ignition sensitivity.

Moreover, some of the operational parameters mentioned above can be altered by external factors affecting thermal batteries during a long period of storage.

Modification of a particular ingredient of a high calorific mixture (for example, Fe powder and/or KClO<sub>4</sub>) resulting from introducing an activator into the latter leads to significant improvement of the efficiency of operation of the thermally activated floating battery.

State-of-the-art designs of thermally activated batteries are presented in the paper.

**Keywords:** reserve batteries, thermal-activated batteries, Zr/BaCrO<sub>4</sub> system, Fe/KClO<sub>4</sub> system.

Chemical sources of electric current, in which the red-ox reaction generates useful electric energy can be described as the primary and secondary cells. The first group includes cells in which the potential chemical energy can be converted into the electric energy only once (e.g. the zinc-manganese alkaline cell). The second type of cells are those in which the energy conversion is reversable (e.g. in the lead-acid accumulator).

A primary cell consists of electrodes made of zinc and of MnO<sub>2</sub>, and the electrolyte is an aqueous solution KOH (35 ÷ 52) wt.% [1].

For the first time, it was applied in early sixties of XX century.

An advantage offered by this type of cell is a possibility of obtaining high current density in the temperature ranging from (-30 ÷ +55) °C. After storing this cell for 4 years at 40 °C, a decrease of its nominal capacity by some 30% takes place, which happens after 8 years if the cell is being stored at 20 °C.

Generally, self-discharging of the primary cell can be fully eliminated by introducing the electrolyte only at the moment when a specific apparatus is to be supplied by the cell. Intensive research on designing such cells, called the reserve batteries, started during the II World War.

Reserve battery is a battery which will not deliver current in its manufactured form until activated by a suitable procedure, e.g. by adding the electrolyte to dry components or by raising the temperature of the cell [2].

With respect to the way of activation and / or the kind of the electrolyte used, reserve batteries can be divided into the following groups:

- water activated, using fresh water (i.e. containing up to 1.2 g dm<sup>-3</sup> mineral components) or seawater;
- electrolyte-activated; using the electrolyte solute or electrolyte solvent;
- gas-activated by introducing a gas into the cell;
- heat-activated, using solid electrolyte which is heated to molten condition.

Time of activation of the reserve battery is the period from the moment of introducing an impulse starting the

activation mechanism until obtaining the right supply parameters i.e. current voltage and intensity.

The thermal battery or heat activated battery is an important class of reserve battery. The salt electrolyte, which is in the solid state the in room temperature and non conductive when the battery is storage. The battery is activated by heating it to a temperature about 350 °C, thus make it ionically conductive and permitting the flow of current. The heat source is built in a compact configuration to give a rapid activation of the battery. The operating temperature of activated battery is usually in the range (-50 ÷ +70) °C. The life of the battery after activation is in the range of (1 ÷ 10) min. (maximum discharge time 2h) and depend on the field of application, but the shelf life of an inactivated thermal battery is typically (20 ÷ 25) years. Major of applications of reserve batteries are: projectiles, rockets, missiles, fuse, mines and nuclear weapons. All heat activated battery cells consist of an element from group I or II of the periodic table of elements as an anode, a fusible salt electrolyte and a metal salt cathode.

**Tab. 1.** Advantages and disadvantages of heat-activated batteries.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>- Long storage life in a “ready” state.</li> <li>- Activation time &lt; 1 s.</li> <li>- Peak power densities &gt; 11 W cm<sup>-2</sup> of electrode.</li> <li>- No maintenance required.</li> <li>- Self discharge is negligible.</li> <li>- Wide operating temperature range.</li> <li>- High reliability and ruggedness.</li> <li>- No out gassing.</li> <li>- Custom designed for specific voltage, start time, current.</li> </ul>	<ul style="list-style-type: none"> <li>- Relatively short activated lives.</li> <li>- Low to moderate energy densities.</li> <li>- Surface temperatures can reach 200 °C.</li> <li>- Voltage output is not linear.</li> <li>- One time use.</li> </ul>

The structure of a thermally activated battery considering also elements not being the electrochemical system. Like in classic cell, the anode is separated from the cathode by the electrolyte which is a good ionic conductor after being molten. Between the cells, there is a heating agent in the tablet form; at the bottom of the battery pile and in its upper part the number of tablets is double. Depending on the applied electrolyte heating system (pyroheater), individual cells are connected by bridges or remain in direct contact. In this first case, a non conductive material is applied as the heating mixture whereas in the other - a good conductor of electric current is used.

In the upper part of the battery, an incendiary agent is placed - an electrically or mechanically started primer which is meant to supply the energy necessary for indirect or direct ignition of the heating mixture (i.e. a tablet). Also, an important element of a thermally activated battery is thermal insulation minimizing heat losses after activation of the battery and making it possible to prolong the time of its functioning, best until the whole active material of one of the electrodes has been used up. All the above mentioned elements of the battery are closed in a tight housing.

**Tab. 2.** Types of heat-activated batteries.

Electrochemical system anode/ electrolyte/cathode	Cell voltage, [V]	Average live time, [s]	Activation time, [s]
Ca/LiCl-KCl/K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2.8 ÷ 3.3	2	0.05 ÷ 0.2
Ca/LiCl-KCl/WO <sub>3</sub>	2.4 ÷ 2.6	70	0.25 ÷ 0.8
Ca/LiCl-KCl/CaCrO <sub>4</sub>	2.2 ÷ 2.6	60	0.35 ÷ 0.7
Mg/LiCl-KCl/V <sub>2</sub> O <sub>5</sub>	2.2 ÷ 2.7	120	---
Ca/LiCl-KCl/PbCrO <sub>4</sub>	2.0 ÷ 2.7	60	0.1 ÷ 0.4
Ca/LiCl-KBr/K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2.0 ÷ 2.5	25	0.1 ÷ 0.5
Li/LiCl-KCl/FeS <sub>2</sub>	1.6 ÷ 2.2	250	0.5 ÷ 1.0
Li(alloy)/LiCl-KCl-LiF/FeS <sub>2</sub>	1.5 ÷ 2.1	600	0.3 ÷ 0.8
Li(alloy)/LiCl-KCl-LiF/CoS <sub>2</sub>	1.5 ÷ 2.0	300	0.3 ÷ 0.8

From the practical point of view, mixtures characterized by low gas emission, called the heating mixtures or pyrotechnical heaters, are of particular interest. Classic high calorific mixtures with low gas emission consist

mainly of powders of metals like Zr, Nb, Mn, Fe, Cr, W, B, Si, Sb i Bi ,or their alloys [3], and oxidants such as  $\text{KClO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{PbCrO}_4$ ,  $\text{KClO}_3$ ,  $\text{CuO}$ ,  $\text{PbO}_2$  or  $\text{Pb}_3\text{O}_4$  [4,5]. Currently, two kinds of low gas high calorific mixtures are practically applied in technology. One of them is the so called heating paper (configuration Zr/BaCrO<sub>4</sub>) being a mixture of the powders of zirconium and barium chromate(VI) deposited on an inorganic carrier, the other being a mixture of the powders of iron and potassium chlorate(VII) applied in the form of a tablet (the so called heating tablet).

The heating paper is prepared by mixing the powders of zirconium of pyrotechnical purity and  $\text{BaCrO}_4$  with grain size below 10  $\mu\text{m}$  with inorganic ceramic or quartz fibers. After adding water to this mixture, a pulp is obtained which is next used for making appropriate sheets employing the technique applied for paper production. The finally obtained product, after thorough drying, is very sensitive to such factors as electrostatic charge and friction. Its rate of burning is 10-300  $\text{cm s}^{-1}$  and calorificity corresponds to ca 1675  $\text{J g}^{-1}$  [6]. The heating paper is original product as well as the product of its combustion, display thermal and electrical insulation properties [4]. It is often used as a tape for ignition of a heating mixture (e.g.  $\text{Fe/KClO}_4$ ) in the form of a heating tablet.

Guidotti studied the effect of the accelerated process of ageing of the configuration Zr/BaCrO<sub>4</sub> applying various temperature values (i.e. 110 °C, 150 °C and 200 °C) as well as the time of storage upon the rate and calorificity of its burning. He found significant decrease of the rate of burning and calorificity of the mixture taking place along with the increase of the temperature and time of storage [7]. In general, the noted disadvantages of the high calorific mixture Zr/BaCrO<sub>4</sub> are: sensitivity to electrostatic charge, sensitivity to shocks generating products of reaction being thermal and electrical insulators, and high cost of zirconium [8].

Heating tablets are obtained by mixing the moisture-free powders of iron and potassium chlorate(VII) of the grain size of 1-10  $\mu\text{m}$ . Usually, the iron powder content in this system ranges from 80 wt.% to 88 wt.% [4]. The mixture shows much lower sensitivity to ignition than the heating paper, however, the tablets prepared from it are much more mechanically resistant to vibration and shock. Considerable excess of the iron powder in the tablet causes its suitable values of electric conductivity and thermal capacity, which permits to extend the effective time of work of the supplied appliance.

Calorificity of the mixture is determined by its chemical composition and it ranges from 920  $\text{J g}^{-1}$  to 1420  $\text{J g}^{-1}$ , and the rate of burning is (1 ÷ 20)  $\text{cm s}^{-1}$ . For example, the mixture containing 16 wt.%  $\text{KClO}_4$  and 84 wt.% Fe heats elements of appliances up to (550 ÷ 600) °C, whereas the stoichiometric mixture releases thermal energy in the amount of ca. 2972  $\text{J g}^{-1}$ , and the final products of its decomposition are KCl and FeO [9].

Studies on the heating material consisting of two mixtures, Zr-BaCrO<sub>4</sub> and Fe-KClO<sub>4</sub>, were carried out with application of an electrolyte being a eutectic mixture  $\text{Li}_2\text{SO}_4$ -NaCl in the chemical sources of electric current. This configuration facilitated effective work of the battery for some 10 min. It was found that application of the mixture Fe-KClO<sub>4</sub> as a heating element in the thermal battery and the eutectic mixture LiCl-KCl with melting point of 352 °C as an electrolyte permitted the battery to work effectively for (10 ÷ 14) min. [10]. For activation of a thermal reserve battery in the electrochemical system [cathode/ $\text{CaCrO}_4$ /electrolyte/eutectic mixture KCl-LiCl-anode/Ca], a heating material was applied consisting of Fe-KClO<sub>3</sub> and Fe-KClO<sub>4</sub>, respectively, obtained by impregnation of the sintered iron powder. Application of iron in this form facilitates obtaining good thermal conductivity which significantly affects the rate of battery activation [11]. Also, the authors of this statement suggested application of the mixture Ni-KClO<sub>4</sub> as a high calorific material in this system. When only one mixture, i.e. Fe-KClO<sub>4</sub> is used probability of the damage to the battery increases, and particularly after its exposition to vibration and/or shock. It was found in two out of five batteries tested [12,13].

Construction of thermally activated reserve batteries containing the calorific mixture Fe/KClO<sub>4</sub> as a heating agent is simpler than that of batteries containing the heating paper, however, some specific requirements have to be satisfied during their manufacturing. This refers to the components of the heating tablet, i.e. potassium chlorate(VI) and iron powder, as well as to the way of preparing the tablet.

It was found that commercially available  $\text{KClO}_4$  was not suitable for making the mixture due to its considerable contamination. Tab. 3 presents the contamination content found in two samples of chemical purity described as "technical" and "analytically pure" - it turned out the contaminations were  $\text{Cl}^-$  and  $\text{Na}^+$  ions.

**Tab. 3.** Main impurities contents in the investigated  $\text{KClO}_4$  (expressed in wt. %).

Sample of $\text{KClO}_4$	$\text{Na}^+$	$\text{Cl}^-$
initial	3.960	0.0088
after first step of crystallisation	0.248	< 0.0005
after second step of crystallisation	0.084	< 0.0005

Application of classic crystallization from an aqueous solution permits to significantly reduce the concentration of the  $\text{Cl}^-$  ions [14]. This process leads also to lowering the content of the  $\text{Na}^+$  ions which in the potassium chlorate(VII) occur as  $\text{NaClO}_4$ . This compound, in normal conditions occurring as a  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  hydrate, is undesirable due to its strong hygroscopic properties. It was found that, during storage at room temperature, tablets of high calorific mixture containing the contaminated potassium chlorate(VI) undergo visible corrosion with formation of the mixture of such compounds as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeOOH}$  which contribute to the loss of activity.

Another issue is dispersion degree of the usually coarse  $\text{KClO}_4$  powder to the grain size ( $1 \div 10$ )  $\mu\text{m}$ . A procedure was elaborated which permitted to obtain grains of this size avoiding the classic disintegration. The grains obtained by this technique are much more stable in the mixture and during its storage at increased temperature their contribution to decreasing the parameters of the high calorific mixture tablets is much smaller than that of grains obtained by classic size reduction.

Iron powder applied in the mixture has the greatest influence on its activity. Results of the thermogravimetric studies of tablets prepared using the iron powders obtained by different methods suggest that the indirectly applied practical chemistry determines mainly their chemical reactivity.

It was found that in some iron powders metallic contaminations occur, such as Mn, Cr or Ti - mainly in their superficial layers. Another reason can be a passivating layer of iron oxide(III) closely adhering to the surface of the metallic iron. This is suggested by results of measurements carried out using the TPR, RS and ICP-MS-LA methods [15]. In order to eliminate the layer of  $\text{Fe}_2\text{O}_3$  from the surface of the iron powder, it was subjected to reduction at ca 300 °C in the dynamic atmosphere of the dihydrogen containing mixture. As a result, a layer of magnetite was formed on the surface of the iron powder, which is easily oxidized causing lowering of the temperature of activation of the heating mixture tablet.

Properties of the high calorific mixture can be altered by introduction of powders of such metals as Mo, Ti, Ni, W or nano-Fe acting as activators.

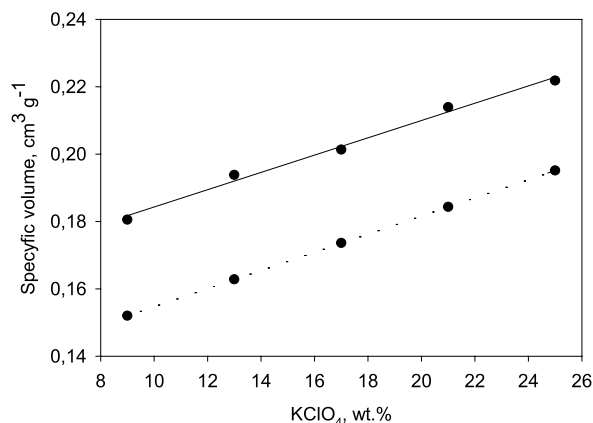
Values of the specific volumes of mixtures of the iron powders carbonyl and electrolytic presented in Fig. 2 and Fig. 3 show dependence of the value of the specific volume for selected mixtures on the function of the  $\text{KClO}_4$  concentration. Specific volume calculated was marked with dash line, experimental values was marked with solid line. Difference in the determined volume values result from different shapes and sizes of the iron powders' grains. Spherical grains characteristic of carbonyl sample give tablets with lower specific volume values in the whole range of concentration of  $\text{KClO}_4$ . Differences are much smaller when it comes to greater content of potassium chlorate(VII).

Results of investigating the reactivity between potassium chlorate(VII) and iron powders with activators in the solid state are given in tab. 1. It has been established that the presence of iron powders leads to a decrease in the temperature of  $\text{KClO}_4$  decomposition by about 160 °C. Adding molybdenum as activator to the mixture containing the iron powder obtained by reduction of an iron compound results in slight lowering of its ignition temperature, while addition of titanium gives the opposite result. After addition of titanium powder to the high calorific mixture containing the iron powder obtained by electrolysis ignition temperature of the mixture goes up. The observed increase in the ignition temperature may be explained by very small amount of  $\text{TiO}_2$  present on the surface of titanium powder studied. Energetic effect resulting from the influence of the components of the high calorific mixture containing the iron powders (i.e. reduced or electrolytic) and the titanium powder increases with the growing amount of activator being added to the mixture. This is caused by greater amount of heat released during reaction of oxygen with Ti than during that with Fe [16].

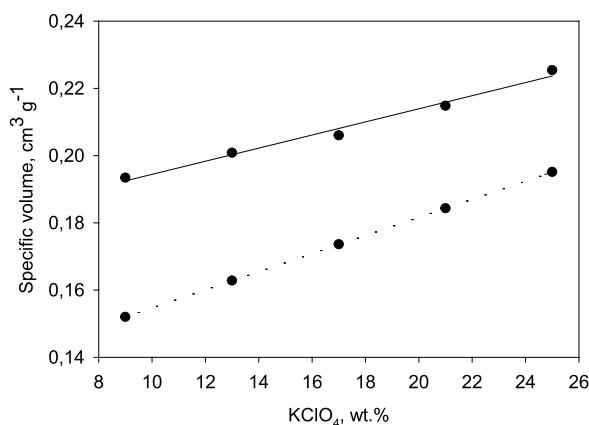
**Tab. 3.** Characteristic of some parameters of high calorific mixtures with  $\text{KClO}_4$  17 wt.% and (Fe + activator) 83 wt.%,

No	Sample symbol*	Content of activator [wt.%]	Initial decomposition temperature [ $^{\circ}\text{C}$ ]	Reaction heat [ $\text{J g}^{-1}$ ]	Burning rate [ $\text{cm s}^{-1}$ ]
1	R	0	445	1115	3.7
2		Mo 1	440	1065	3.6
3		Mo 2	433	1079	4.2
4		Mo 3	440	991	4.9
5		Mo 4	433	983	6.3
6		Mo 5	430	952	7.4
7		Ti 1	477	1076	3.8
8		Ti 2	476	1081	---
9		Ti 3	477	1091	4.5
10		Ti 4	468	1198	6.0
11		Ti 5	469	1236	5.6
12	E	0	457	1175	2.2
13		Mo 1	378	1140	2.0
14		Mo 2	361	1149	2.5
15		Mo 3	365	1069	2.7
16		Mo 4	365	1106	2.4
17		Mo 5	365	1109	2.4
18		Ti 1	468	1140	2.2
19		Ti 2	469	1175	2.9
20		Ti 3	465	1279	3.4
21		Ti 4	469	1382	5.5
22		Ti 5	465	1478	6.0

\* - R- reduced iron powder, E- electrolytic iron powder

**Fig. 2.** Specific volume of Fe- $\text{KClO}_4$  mixture in function of  $\text{KClO}_4$  concentration for iron carbonyl sample.

The opposite direction of changes was noted after the molybdenum powder had been added as activator. Along with the increase of the activator (Mo) concentration, amount of the energy released in the high calorific mixture containing the reduced iron powder was considerably decreasing. In the mixture with the main component being the iron powder obtained by electrolysis the influence of this activator upon the energetic effect was much weaker released energy registered by the thermogravimetric method (DTA/TG) are slightly higher than those obtained by calorimetric measurements. In general, employment of the thermogravimetric method allows to simultaneously determining the ignition temperature, calorificity and the amount of gases released to the atmosphere from the high calorific mixture under investigation.

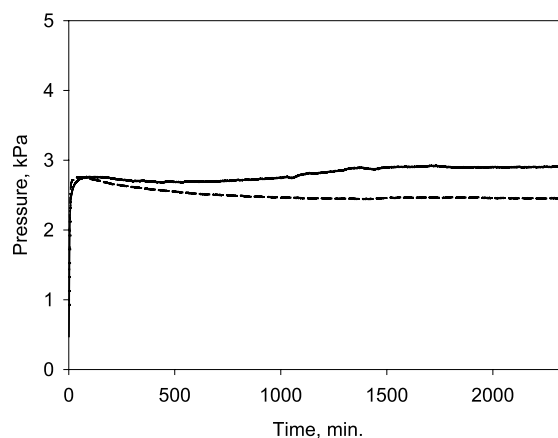


**Fig. 3.** Specific volume of Fe-KClO<sub>4</sub> mixture in function of KClO<sub>4</sub> concentration for iron electrolytic sample.

Values of the research was also conducted on the accelerated ageing of a high calorific mixtures containing 83 wt.% of reduced iron powder with 17 wt.% of KClO<sub>4</sub> and 79 wt.% of iron powder denoted as R, 4 wt.% of molybdenum, 17 wt.% of KClO<sub>4</sub> (see Fig. 4). Increase of pressure noticed during the first stage is caused by removing from the sample surface small quantities of water introduced there during placing the sample in the appliance. During the above experiment, the high calorific mixture with no activator contained does not show any significant changes of pressure. When molybdenum is added to the mixture as an activator slight lowering of the pressure takes place, which can be explained by sorption of the contained quantities of oxygen and/or water vapor from the atmosphere surrounding the analyzed sample. A drop in pressure after 500 min. of the experiment and subsequent return to the initial pressure value after 1250 min. are difficult to interpret.

It was found that storing pellets of heating mixture (with activator and without one) for 12 months at 50 °C in inert atmosphere containing < 10 ppm H<sub>2</sub>O and < 0.5 ppm O<sub>2</sub> did not affect its basic properties such as burning rate, calorificity and sensitivity to ignition (2 J mm<sup>-2</sup>).

Improper preparation of the tablet with the use of the above mentioned components results in significant technical problems during pressing its ingredients and ignition. Besides, occurrence of dimensional instability of the tablet after activation is possible as well as low calorificity and decrease of chemical reactivity after some longer time of storage even at room temperature.



**Fig.4.** Thermal stability of Fe-KClO<sub>4</sub> mixture: 83 wt.% Fe-reduced – solid line, 79 wt.% Fe-reduced and 4 wt.% Mo – dash line.

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