

AL10 - State and Development Prospects of Technologies for the Use of Unshaped Lining Materials in Aluminum Reduction Cells

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Abstract

The paper elaborates on the use of unshaped lining materials in modern aluminum cells and lists the technical parameters of the main types of unshaped materials. It demonstrates the main elements of an up-to-date cell lining technology that uses un-shaped materials. The paper also compares conventional cells using bricks with cells using unshaped materials and lists several process and economic advantages of unshaped materials over conventional bricks. Moreover, it has been proved that such parameters as service life, power consumption, current efficiency, amount of waste and lining duration tend to remain stable with an increase in the number of cells. Autopsy results for cells older than 2 200 days are given. Furthermore, the paper provides information on material transformations during cell life and in case of abnormalities. In conclusion, it is demonstrated how said cell lining technology and equipment can be further enhanced, including technical solutions regarding developing cathode designs ensuring minimum waste.

Keywords: Aluminium electrolysis cells, unshaped lining materials, cell design and performance, equipment for installation and compaction lining materials, autopsy.

1. Introduction

The cost of aluminium production is one of the main factors to determine the competitiveness of companies in the aluminium industry. The reduction of cost of overhauls, storage or disposal of waste generated helps to lower the cost of aluminium production. This is why the search for new, more efficient, lining materials for cathodes in electrolysis cells and their application technologies continues in the countries with primary aluminium production.

Traditionally, shaped products in the form of bricks of various sizes, mainly aluminosilicate, are used as barrier materials to protect lower-lying thermal insulation materials in the design of cathode electrolysis cells [1]. This is primarily due to the properties of the resulting products of interaction with fluorides and sodium vapours. Advanced high-quality barrier bricks for aluminium electrolysis cell cathodes have low apparent porosity (up to 13 %) and small pore sizes to reduce the penetration of aggressive gaseous and liquid components into the thermal insulation layers. However, the gas permeability of the barrier brickwork is generally determined not by the properties of the shaped products, but mainly by the condition of the joints [2] between them.

The refractory mortar used to seal the joints is the material used to make masonry mortar and although it has a material composition close to the bricks, it is vulnerable to fluorides and

aggressive gases, such as sodium vapours and sodium tetrafluoroaluminate. This is primarily due to the fact that it is not as dense as fired bricks. Cryolite-resistance tests have shown that the joint material has a resistance of no more than 50 % in relation to brick resistance [3].

In addition to shaped refractory materials, significant experience has now been gained in the use of unshaped lining materials of various particle size and mineral content, which allow producing seamless layers. As compared to shaped products, the technology for producing such materials requires 2–3 times less space of production facilities and is characterised by higher productivity (4–5 times) and 5–6 times lower energy costs [4].

In the previous development stages of the aluminium industry, alumina was widely used as a lining material [5]. There was the possibility of recycling it in the electrolysis cells or reusing it as lining materials, which reduced the amount of waste. However, as electricity costs rose and the composition of the electrolyte changed, alumina was replaced by insulating materials, diatomite and vermiculite, which were protected from above by an aluminosilicate-based unshaped refractory material with specially selected chemical and mineral and disperse compositions. Several types of such materials are currently known: a mixture of aluminosilicate [6], anorthite [7], and olivinic [8] compositions. Laboratory and industrial tests show that dry barrier mixes (DBM) based on aluminosilicates with a carefully selected particle size distribution have an advantage over others due to the ability to make viscous glass barriers [9]. At the same time, the performance of electrolysis cells with unshaped materials is generally close to that of electrolysis cells with brickwork. The successful DBM use is supported by data on the international practice [10]. Thus, the average service life of 300 kA electrolysis cells installed in China using the DBM is 2 200 days [10].

The subsequent compaction of unshaped lining materials (USLM) is an essential element of their application technology when assembling aluminium electrolysis cell cathodes. The easiest way of compacting the USLM is by using ordinary rollers [11]. However, the structure of the lining material did not have the required low porosity and small pore sizes. Although increasing the density of compacting (up to 25 %), the rollers fitted with a vibratory mechanism caused a wave-shaped defect in the surface. The method of lining the cathode device of the aluminium electrolysis cell is known to include filling the powdered material into the cathode cover of the electrolysis cell and levelling it with a straight edge. The lining was compacted by pneumatic tamping from above through a hot rammed carbon mass [12]. However, there has been a reduction in the service life of the electrolysis cells. When compacting the material by the dynamic method using a slide with a vibrator, both compaction and decompaction processes took place at the same time, resulting in dusting of the material being compacted [13]. Compaction of unshaped materials is most often performed using vibratory plates, which are used in construction technologies. The main disadvantage of this method of lining is the need for vibratory plates to pass through the surface of the barrier material multiple times in the cathode unit due to the small size of the plate. The parameters of the resulting barrier layer depend on the qualifications and conscientiousness of the operator. However, the most significant disadvantage is that the operation of the vibratory plate is mainly based on a dynamic shaping method with sub-optimal amplitude frequency and weight characteristics. With a low bulk density of the lining material, this results in both compaction and decompaction processes occurring at the same time. This results in dusting of the material being compacted.

In general, it can be noted that the use of unshaped materials in the installation of electrolysis cell cathode devices differs favourably from the use of the bricklaying technology due to the absence of joints, reduced installation time for lining materials, and lower labour costs [14]. The reduced installation time is particularly beneficial for production facilities repairing electrolysis cells in potrooms. However, these technologies have been generally implemented only for upper, refractory, lining layers, which are placed on thermal insulating bricks or vermiculite slabs. With

the exception of alumina, there is no experience of using unshaped lining materials in the entire under-cathode space. As a result, the attempts to improve both the unshaped materials themselves and the technologies used in their application seem relevant. The purpose of this work is to show some results of research and development carried out by the RUSAL engineers to reduce the production costs through the use of unshaped lining materials and technologies for their application in aluminium electrolysis cell cathodes.

2. Experimental Work

The diffractograms were obtained with the Philips PW1800 x-ray diffractometer. The quantitative identification of x-ray phases was carried out using the phase identification information retrieval system [15] and the inorganic phase and mineral x-ray reference database [16], including 115 000 standards. The cyanide content was determined in the specialised environmental laboratory (Center for Laboratory Analysis and Technical Measurements) according to a methodology (PND F 16.1:2:2.2:2.3:3.70-10), using a photometric method with pyridine and barbituric acid [17].

2.1. Experimental Part: Field Tests of Vibratory Plates

At the first stage of the development of the unshaped lining technology, comparative tests were carried out on 2 types of vibratory plates, A and B. This was traditional equipment for carrying out small-scale construction repair operations: the compaction of asphalt concrete mixes and grain material. The vibratory plates were tested when compacting dry barrier mix E 50 on one of the cathode shells of electrolysis cell C 255. The height of the uncompacted layer was 115 mm. The test results showed that when treated for 1.5 hours with additional material being loaded by a worker, the average height of the compacted dry barrier mix layer over the area to be treated decreased from 115 to 87.6 mm. This was in line with a reduction in the porosity of the resulting layer to 22.2 %. While using another vibratory plate A, the DBM layer could only be compacted to 90.2 mm, which corresponded to 24.3 % porosity. For comparison, standard ShB bricks have an apparent porosity of about 22 % and similar overseas products of even 12–13 %.

The results obtained were thus far removed from those of shaped products, and therefore the aim was to develop more efficient devices for compacting unshaped lining materials of different height.

2.2. Experimental Part: Industrial Compactor Development

In the course of research and development work, specialists of LLC RUSAL ETC, together with employees of the Institute of Mining of the Siberian Branch of the Russian Academy of Sciences, created a fundamentally new vibratory dry barrier mix compactor (VDBMC) that combines both static and dynamic compaction methods. It included a drive and sealing devices for static processing, made in the form of a motorised roller and a dynamic processing unit connected to the roller. VDBMC overall dimensions: 670 x 3200 x 680 mm. VDBMC weight: 2 150 kg. The direction of travel was controlled by changing the shaft speed of one of the gear motors.

Experimental studies have established the dependencies of density, as the main parameter of DBM compaction, on the operation mode of vibrating exciters (shock or shockless), as well as on the magnitude of vibration acceleration and the weight of cantledges. The studies also assessed the condition of the lining materials after the compaction operation. Since vibrating compaction after reaching the maximum density can cause the material to decompact (loosen), the task was to determine the time of compaction to a given density. The selection of the device speed is also related to this issue.

Experimental studies were carried out on a bench, which is a mock-up of a cathode device made as a platform with dimensions of 1.51 x 1.57 m. The lining of the site was similar to the lining of the electrolysis cell base: two layers were made of insulating bricks and two more layers were made of fireclay bricks, the upper row of which was laid on a refractory solution. The expansion joints were filled with a fireclay crushed material; the masonry layers were covered with a fireclay powder. E50 grade DBM was used as a compacted medium, which was laid in accordance with the regulatory documentation. DBM bulk layer parameters: thickness 122 mm, bulk density 1.57 kg/m³, and backfill weight 457.5 kg. Before each experiment, the site was refilled with a dry barrier mix and levelled, which means a strip of equal pre-density and even surface was prepared. In order to determine the optimal mode of vibrating the working body in which the DBM compaction process is carried out with the highest possible density, as well as to find out the impact of accelerations on the dynamic compaction process, the experiments used pneumatic vibration exciters with different amplitude and frequency characteristics, operating in both shock and shockless modes. The accelerations and vibration frequency of the working body were measured using piezoaccelerometers of type KD 35 and vibration measuring equipment. The density of the material at fixed points was determined based on the changes in the volume of the DBM being compacted. Measurements of both acceleration and density were made multiple times and the results were averaged.

The analysis of the results obtained showed that with the DBM compaction the shock mode of the vibrating exciters is more efficient. The results of experimental studies have shown that the density of material increased with the acceleration of vibrations of the working body. However, the resulting high dynamic loads have a negative impact on both the VDBMC design elements and the lower lining elements.

As the speed of the device increased, the density of the material being processed expectedly decreased, as the time of static and dynamic exposure decreased. However, a decrease in the density of the medium being treated was also observed, when the speed of movement of the device decreased relative to a certain value, at which the maximum DBM density was observed. This can be explained by the effect of decompaction. It is known that as the time of exposure increases, the material may become loose once it reaches its maximum density. Thus, it was determined that there was an optimum speed of movement of the device in the vibration modes considered.

As experiments have shown, the vibrator cantledges increase the compaction process efficiency. By using cantledges, a given density of material can be achieved at higher speeds. When the device was operated without cantledges, the DBM density was 1 980 kg/m³, and that with cantledges was 2 120 kg/m³, all other conditions being equal. It should be noted that the optimum speed of the device was selected in accordance with the condition of obtaining the required productivity of the DBM compaction process. The unit was made on an industrial scale and successfully passed all types of tests. However, as the experience of using the unit at the production facility has shown, the disadvantage of the unit was the dependence of the degree of compaction on the air pressure in the supply lines of the production facility. Therefore, a unit with electric vibrators was developed as a vibratory compactor of dispersed materials (VUDM). Compactor (VDMC) was developed. Improved unit can operate in two design options: the basic version with electric vibrators and the optional version with pneumatic vibrators. In the course of subsequent operation, the main advantages of the developed VDMC unit were identified and confirmed in comparison with the VDBMC and known vibratory plates:

1. The total porosity of the compacted E-50 SBS layer is 17–18 %, which is 5–8 % lower than that of the vibratory plate compacted DBM layers.
2. The unit's operation is automatic and does not depend on the operator's skill.
3. There is practically no dusting during the unit's operation.
4. The unit has a modular design, which makes it possible to adapt it to the installation of electrolysis cell baths of different widths.

5. The unit can operate in strong magnetic fields.
6. After compaction, workers can move freely on the compacted layer without any risk of damage.

Many years of experience of the VDMC unit operation made it possible to create a VDMC compactor designed for compacting unshaped materials of great thickness; the design of the compactor (Figure 1) is patented in the USA [18], Canada [19] and China [20].

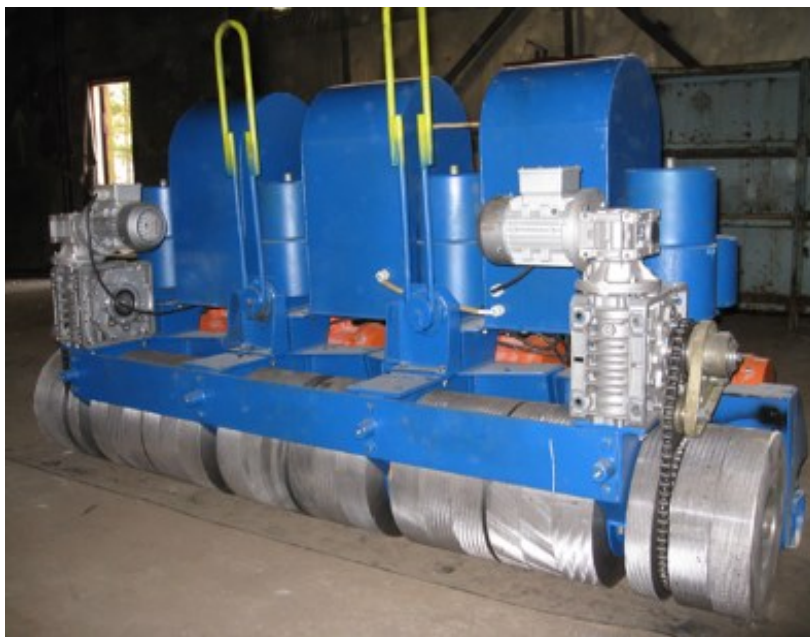


Figure 1. General view of the compactor.

2.3. Experimental Studies in an Industrial Cell

For a number of years, RUSAL has been working on developing new resource-saving cathode lining technologies. The main stages of this work are reflected in cathode lining designs with unshaped materials (Figure 2). The first cathodes A had a small thickness of barrier materials, but the maximum LSC and crown thickness. A total of 3 electrolysis cells were lined, one of which was autopsied after 894 days. The autopsy showed that 80 % of LSC waste material could be recycled, but showed a sufficiently high concentration of cyanides directly under the DBM, comparable to that of cyanides in the basement blocks. The autopsy outcome was discussed at the ICSOBA 2016 conference [21]. The results of an autopsy of cathode A (Figure 3), which operated for 2 338 days, showed an abnormally small lens thickness and the crumbly nature of the material under the DBM. Type A cathode samples were oily black and could be easily destroyed. The analysis showed (Table 1) that they contained predominantly carbon and sodium carbonate. Below, durable plates with a thickness of 50–70 mm were found. In the lowermost part, at a distance of 100 mm, the semi-coke samples were practically unchanged. An important factor is that the low density allows for their recycling. Modification of the cathode by increasing the height of barrier materials (group B cathodes) allowed reducing the cyanide content to 2–3 ppm, but increased the amount of second-cut spent potlining (SPL-2). Following the development of special equipment for the installation of unshaped materials across the full width of Cathode C, SPL-2 was minimised. The latter was facilitated by the use of burnt clays: natural clays fired by an underground fire in fossil coal beds. Thus, the optimum ratio between the height of the refractory (barrier) and heat-insulating layers in the cathode makes it possible to achieve a minimum amount of SPL-2 and a recycled carbon material with properties that cause no harm to the environment.

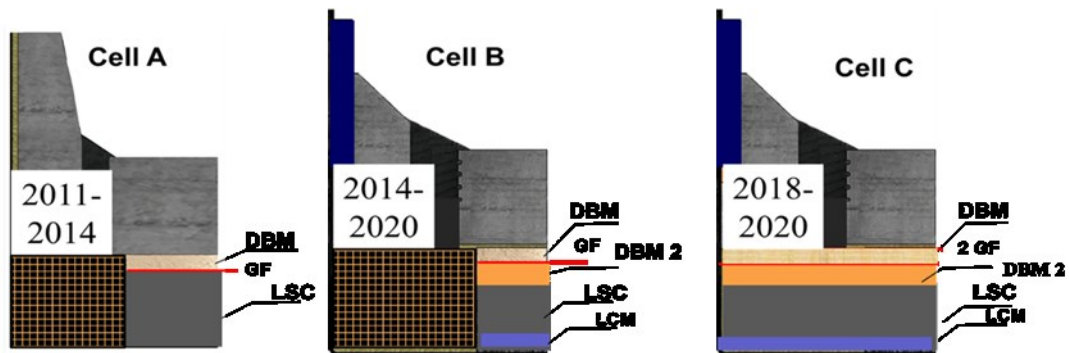


Figure 2. Main cathode device schemes with USLM.



Figure 3. General view of cross-section of central part of cathode A.

Table 1. Phase composition, wt %.

Chemical Formula	Mineral	Peripheral zone		
		8 upper	8 middle	8 bottom
C*	Carbon	60.7	79.4	80.5
NaF	Sodium Fluoride	0.14	0.12	0.14
Na ₂ CO ₃	Natrit	23.6	13.3	10.9
Na ₂ CO ₃ ·H ₂ O	Thermonatrit	12.3	6.03	7.53
CaCO ₃	Calcit	0.88		
CaMg(CO ₃) ₂	Dolomit	1.71	1.0	0.73
SiO ₂	Quartz	0.28		
SiO ₂	Cristabalite	0.15	0.04	0.06

*Defined by the gravimetric method.

3. Discussion

An analysis of the current status of cathodes in terms of minimising financial costs shows that the cost depends primarily on the cathode design. There is trend towards a continuous increase in the cell amperage, and therefore in the size of the cell bottom. Thus, it is becoming increasingly important to reduce labour costs when installing cathodes. Mechanisation of assembly processes shortens its time and improves the quality of work. Continuous growth in energy costs drives the desire to reduce the cost of lining materials and the starting preheat process, while maintaining the stable working and physical properties of the lining materials during their service life is a source of energy savings and long service life. In turn, the service life determines the amount of waste generated to be recycled. The trend towards shorter service life with increasing cell

amperage due to local wear and tear on the cell bottoms leads to an increase in the amount of waste.

In our opinion, there is a factor that can have a positive impact on all of the above items of expenditure. This is the lining weight in the cathode. Indeed, when the weight of lining materials per unit of cathode space is reduced, cathode assembly and disassembly operations are facilitated, the amount of waste generated is reduced, the installation costs are reduced, the accumulation losses during cathode preheating at start-up are reduced, and the cost of purchasing new materials is reduced. The experience of utilising electrolysis cells at RUSAL has shown that one of the ways to reduce the cathode weight is to use pyrolysis products from carbon raw materials. Such products may be lignite semi-coke (LSC), charcoal, or cereal stem pyrolysis products [21, 22]. These unshaped lining materials are characterised by prevalence, low cost, and possibility to use mechanisation means when handling them, including for recycling.

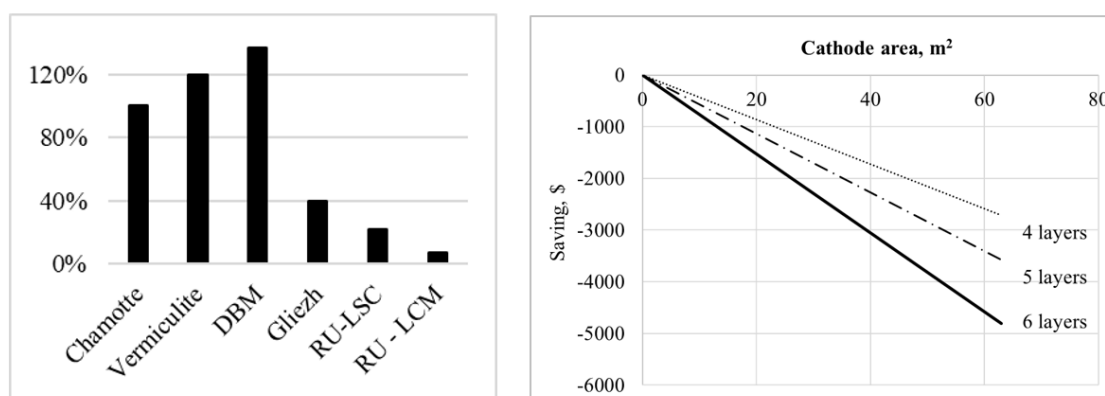


Figure 4. Relative cost of materials per 1 m³ (left) and cost effectiveness of replacing traditional brickwork with USLM (right).

The economic efficiency of USLM application depends on both the price of the material and its density. The left side of Figure 4 shows the relative cost of filling a unit of an under-cathode space. The cost of filling 1 m³ with fireclay bricks is taken as 100 %. As can be seen from the figure, the USLM cost based on pyrolysis carbon is several times lower than that of fireclay.

The greater the amount of standard materials (fireclay and vermiculite) that are replaced by the USLM, the higher is the economic efficiency of the lining replacement measure. Therefore, as the cathode size grows, more and more funds can be saved. At the same time, the bigger the height of the under-cathode space, the higher is the efficiency, too. As can be seen from the right figure, for electrolysis cells with a cathode area of 60 m², replacing six-layer brickwork made of fireclay and vermiculite with unshaped lining materials can save around USD 5 000.

The same pattern is observed for the weight of waste generated. As shown in Figure 5, replacing brickwork with USLMs reduces the weight of lining materials. Whereas for the cathode design with 4 layers of bricks this reduction is just over 5 %; for the replacement of 6 layers of bricks, this reduction is already almost 36 %. This is due to the much lower density of USLM materials. At the same time, it is worth mentioning the highly porous aluminosilicate materials based on burnt clays fired by underground fires in fossil coal beds. In other words, these are clays that have been heat treated under natural conditions.

Monitoring of groups of experienced cells and conventional cells did not show significant deviations in the main indicators of the KPI (Figure 6).

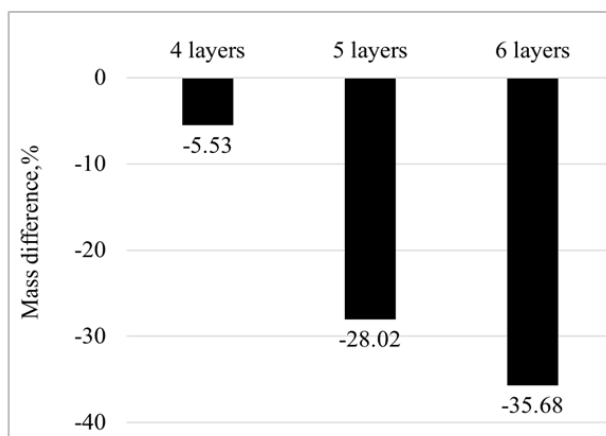


Figure 5. Difference in weight of cathode with USLM and cathode brickwork.

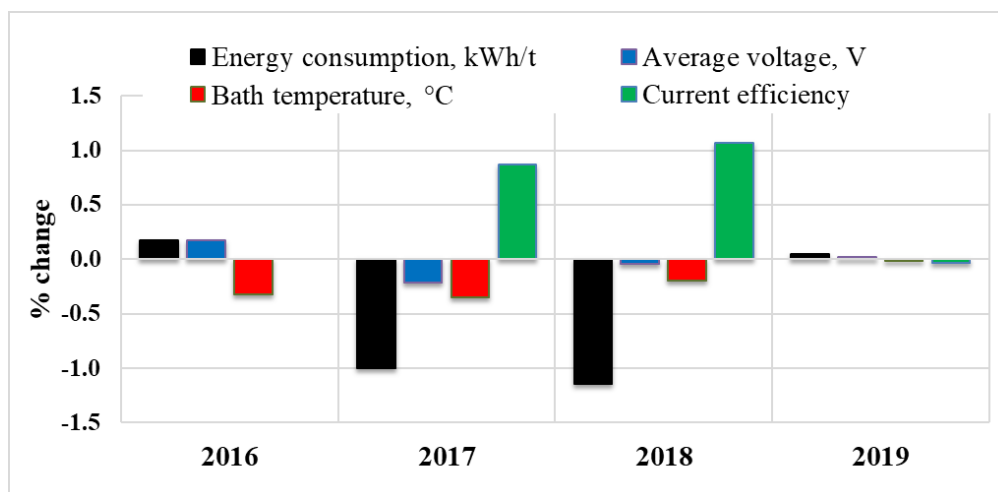


Figure 6. Average annual KPI deviations of test cells from conventional.

Table 2 shows the average annual temperatures and CR values. The stability of the electrolyte composition due to more tightness properties of the barrier materials and its lower temperatures in cathodes with USLM are likely to result in lower aluminium fluoride consumption. However, this requires additional evidence.

Table 2. Changes in average annual aluminium fluoride consumption rates.

Parameter	Annual average for 2016			Annual average for 2017			Annual average for 2018		
	pilot	conv.	delta	pilot	conv.	delta	pilot	conv.	delta
Consumption of AlF ₃ , kg/t	13.5	17.6	-4.1	12.4	15.7	-3.3	15.9	19.0	-3.1
Bath temperature, °C	955.3	958.4	-3.1	954.1	957.4	-3.3	951.4	955.2	-3.8
Bath ratio	2.29	2.33	-0.04	2.29	2.29	0.00	2.28	2.3	-0.02

Continuous monitoring of the status of cathodes with USLM, more than 10 autopsies of electrolysis cells with different service life, analysis of cathode performance parameters, and actual cost reduction in the overhaul of electrolysis cells have led to a rapid growth in the number of electrolysis cells of the RUSAL company operating using this technology (Figure7).

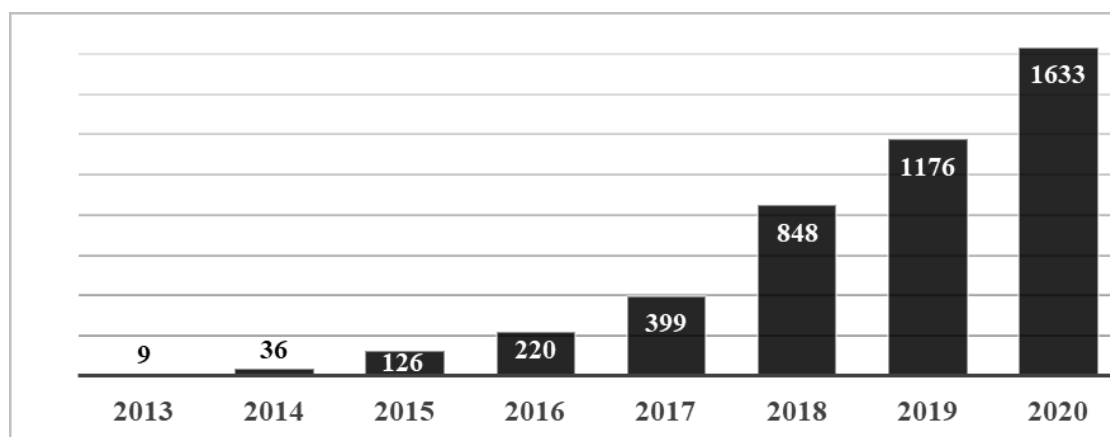


Figure 7. Number of cells of the RUSAL company lined with USLM.

4. Conclusions

The developed resource-saving technology for lining the sub-cathode zone of the aluminum reduction cell with new un-shaped lining materials, based on pyrolysis products from carbon raw materials and the developed lining equipment help reduce the amount of lining materials to be used (due to re-cycling), reduce financial and labour costs for lining, and reduce the amount of SPL-2.

The developed cell lining generates no cyanides, high cell KPIs, and stable thermal and physical parameters.

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