

Long-Term Material Balance of Phosphorus in Aluminium Reduction Cells

^aV. DANĚK, ^aM. CHRENKOVÁ, ^aA. SILNÝ, ^bM. STAŠ, and ^bM. KONIAR

^a*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
SK-842 36 Bratislava, e-mail: uachdane@savba.sk*

^b*Slovalco, a.s., SK-965 63 Žiar nad Hronom*

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The content of phosphorus in input and output materials used in aluminium reduction cells of the Slovak producer Slovalco, a.s. was followed during a three-year period. On the basis of the obtained data the material balance of phosphorus in individual years was made in order to evaluate the trends in phosphorus content in the input and output materials and to understand the reasons of the observed trends.

Phosphorus, like other impurities in the aluminium electrolysis, is an undesirable electrolyte admixture. Impurities are introduced into the electrolyte during electrolysis through alumina, anode materials, as well as the next input raw materials used as additives. Due to the improvements of the Hall—Héroult process during the last two decades, especially at the substitution of the Söderberg anodes by the prebaked ones and the recycling of materials, the accumulation of impurities in the cells becomes one of the most serious problems.

The presence of impurities affects the electrolysis in different ways. Due to the reactions with electrolyte components they may cause change in electrolyte composition and due to the in general lower decomposition potential they decompose on the cathode, thus lowering the current efficiency of the electrolysis and the purity of the produced aluminium. The content of some impurities may be dramatically increased by the use of alumina going through dry scrubber, in which the substantial part of gaseous exhalations is gathered.

To the most frequently followed impurities belong phosphorus, iron, silicon, and vanadium. Especially the content of phosphorus in the produced aluminium plays a crucial role in the usage of aluminium in the engine block casting. Aluminium for such purpose must not contain more than 8 ppm of phosphorus otherwise it becomes brittle and for that use not acceptable.

In the present work the content of phosphorus in input and output materials used in Slovalco, a.s., Žiar nad Hronom, Slovakia, in the period of 1997—1999 has been examined by means of the statistical analysis method. On the basis of the obtained data the material balance of phosphorus in individual years was made in order to evaluate the trends in phosphorus content in the input and output materials and to understand the reasons of the observed trends.

RESULTS AND DISCUSSION

The material balance of phosphorus was performed on the basis of the results of phosphorus oxide and phosphorus analyses in input and output materials. The phosphorus oxide content was followed in primary and secondary aluminium oxide, in aluminium fluoride, and in fresh and recycled electrolyte. The phosphorus content was analyzed in prebaked anodes, in anode butts, and in produced aluminium. By means of the statistical analysis method average data on phosphorus content related to 1000 kg of produced aluminium were calculated.

The basic information needed for the material balance calculation for one average 230 kA pot consisted of the following items:

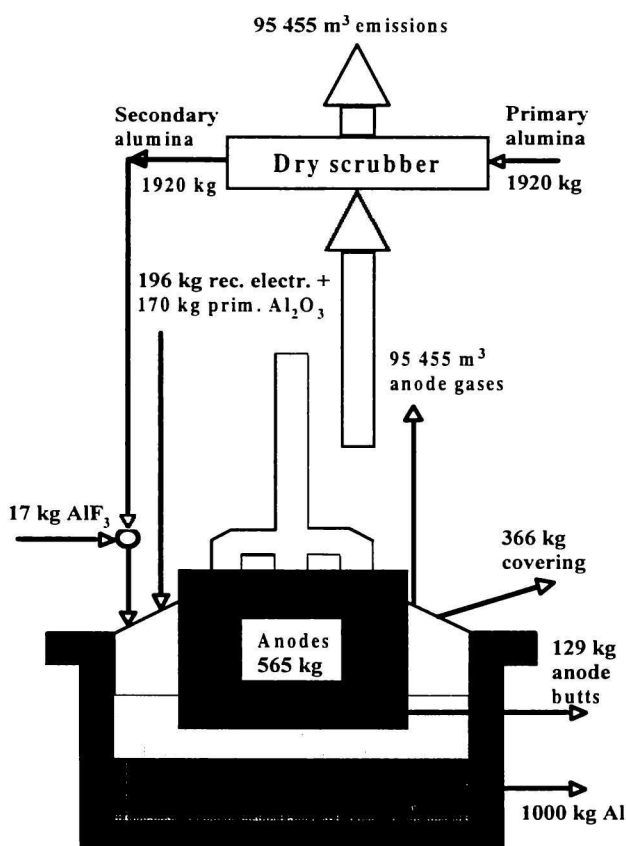
- amount of produced Al (kg),
- amount of exhausting gases (m³),
- covering for one anode consisting of:
 - a) amount of recycled electrolyte (kg),
 - b) amount of primary alumina (kg),
- number of exchanged anodes,
- mass of an average anode (kg),
- amount of consumed alumina (kg),
- amount of consumed AlF₃ (kg).

These basic input and output data were taken from Slovalco, a.s., Slovakia. They changed a little from year to year. The amounts of input and output materials for a daily production of 1000 kg of aluminium in 1999 for one average 230 kA pot are schematically shown in Fig. 1.

In order to relate the material balance to 1000 kg of produced Al, the amount of exhausting gases and the covering of one anode have to be divided by the daily Al production in tons. The anodes consumption

Table 1. Daily Amounts of Input and Output Materials Used for One Average 230 kA Pot in Individual Years

Material	1997	1998	1999
Produced Al/(kg day ⁻¹)	1760	1750	1740
Consumed alumina/(kg/t Al)	1920	1920	1925
Exhausting gases/(m ³ day ⁻¹)	168 000	168 000	168 000
Consumed AlF ₃ /(kg/t Al)	17	15	13
Covering for one anode/(kg day ⁻¹):			
recycled electrolyte	345	325	300
primary oxide	299	280	260
Number of exchanged anodes	1.035	1.07	1.07
Average anode mass/kg	862	872	874
Recycled anode butts/(kg/t Al)	90	116	130

**Fig. 1.** Material balance in the 230 kA pot related to the production of 1000 kg Al.

is given by the number of exchanged anodes multiplied by their average mass.

The mass of covering was calculated as the sum of the amount of recycled electrolyte and primary alumina per 1000 kg of produced aluminium divided by the daily Al production in tons. The average content of phosphorus in the covering was calculated as the weighted amount of phosphorus in both input materials.

Samples for analyses were taken off in three different time intervals: almost every day, once a week, and once a month. In order to obtain unique time axis in

the interval $\langle 0, t, 1 \rangle$ the relative time of analysis was calculated as the ratio of the day, week or month and their sequence number in the year.

For every input and output material the average P₂O₅ (respectively phosphorus) content and the standard deviation of the median for the followed time period was calculated. Besides that, the annual trend as well as the trend over the whole followed time period was calculated using the linear regression analysis. The trend represents the tangent in the P₂O₅ or P content *vs.* the relative time plot. The average content is shown in the figures by dashed line, while the solid ones show the trends.

All needed data but the phosphorus content in exhausting gases were available. This value was estimated from the phosphorus difference in primary and secondary alumina and the difference in the total material balance. It was assumed that the whole difference of phosphorus amount in primary and secondary alumina was transported by exhausting gases to the dry scrubbers, where 95 % was adsorbed and 5 % went out into the atmosphere as emissions.

The total material balance in individual years, *i.e.* the difference between the phosphorus amounts in input and output materials should be equal or near to zero, if the balance has been made correctly. The daily amounts of input and output materials used for one average 230 kA pot in individual years are given in Table 1. The average content of P₂O₅, resp. P, in the individual materials and the annual trend in the three-year period are given in Table 2 and graphically shown in Figs. 2–6. The calculated amounts of phosphorus in input and output materials related to 1 ton of produced aluminium in individual years are given in Tables 3 and 4, respectively.

Statistical Analysis of Phosphorus Content in 1997

The content of P₂O₅ in primary alumina in 1997 was (8.6 ± 1.3) ppm (Fig. 2), however, it shows a rather low variation. The statistically significant increase by 3.8 ppm was obviously caused by the producer.

PHOSPHORUS IN ALUMINIUM

Table 2. Summary of the Statistical Analysis of Phosphorus Content in the Period 1997—1999

Material	1997		1998		1999		1997—1999
	<i>w</i> (mean)	<i>w</i> (trend)	<i>w</i> (mean)	<i>w</i> (trend)	<i>w</i> (mean)	<i>w</i> (trend)	<i>w</i> (trend)
	ppm	ppm year ⁻¹	ppm	ppm year ⁻¹	ppm	ppm year ⁻¹	ppm year ⁻¹
Primary alumina	8.6 ± 1.3	+3.8	10.1 ± 1.3	+0.2	8.3 ± 2.0	-3.9	-0.2
Secondary alumina	75 ± 18	-	(60)	-	43 ± 10	+3	-13
Aluminium fluoride	209 ± 21	+40	212 ± 23	-25	177 ± 33	-91	-21
Prebaked anodes	2.7 ± 0.5	-0.2	2.3 ± 0.9	-0.3	4.4 ± 2.4	+2.0	+1.0
Fresh electrolyte	90 ± 43	-43	99 ± 67	+156	156 ± 32	+34	+34
Recycled electrolyte	215 ± 44	-41	275 ± 50	+53	185 ± 28	-20	*
Produced aluminium	3.5 ± 0.6	-0.6	4.3 ± 0.8	+4.4	6.5 ± 0.5	+0.2	+1.6

* Until 1 August 1998 +53 ppm year⁻¹, then -107 ppm year⁻¹.

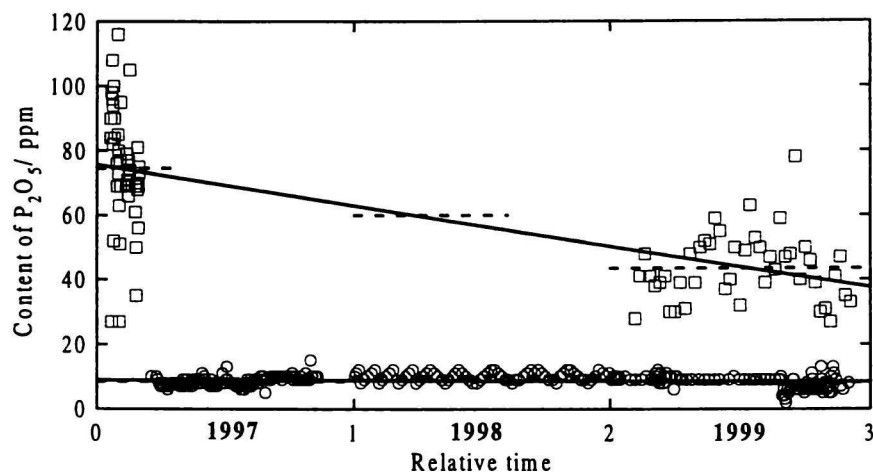


Fig. 2. Content of P₂O₅ in primary (○) and secondary (□) alumina in the period 1997—1999. Dashed lines: trend in individual years, solid lines: trends in the whole period.

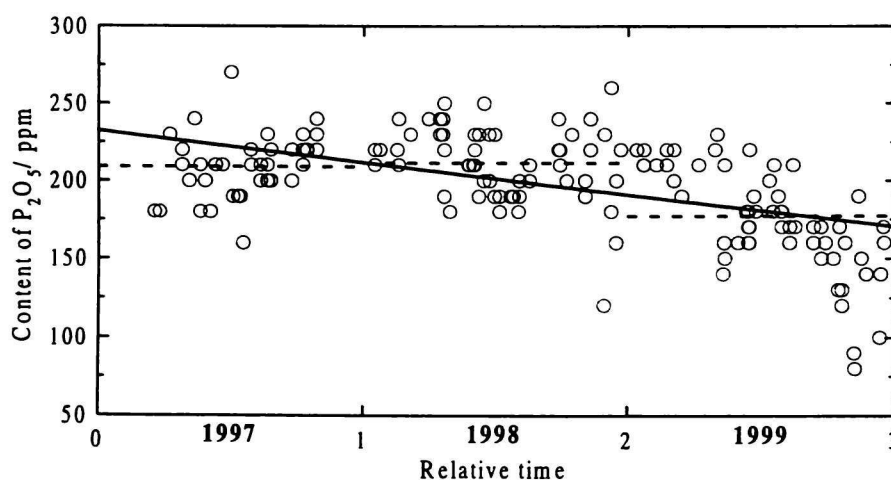


Fig. 3. Content of P₂O₅ in aluminium fluoride in the period 1997—1999.

The average P₂O₅ content in secondary alumina was (75 ± 18) ppm (Fig. 2). However, the analyses were made only in the period from January to March, which is too short to calculate the annual trend. The total phosphorus amount difference per 1 ton of pro-

duced aluminium between primary and secondary alumina is 56.1 ppm P₂O₅. It was supposed that 95 % of this difference was adsorbed in dry scrubber and 5 % escaped as emissions.

Relatively high, (209 ± 21) ppm, is the average

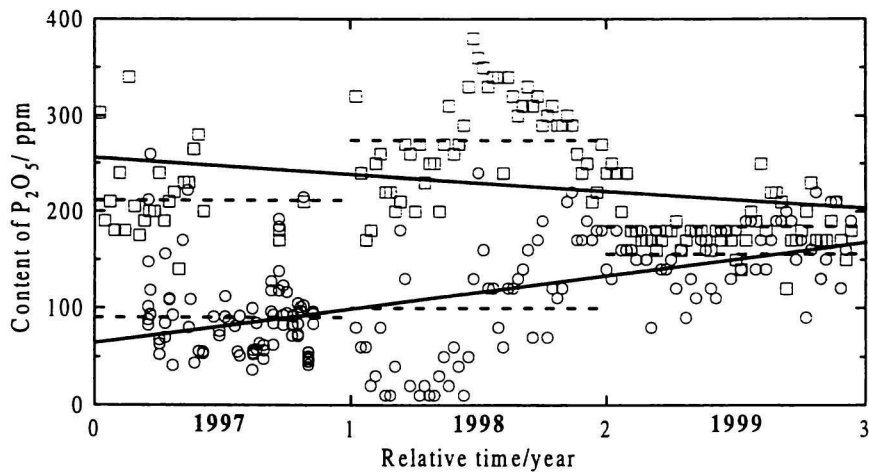


Fig. 4. Content of P_2O_5 in fresh (○) and recycled (□) electrolyte in the period 1997—1999. Dashed lines: trend in individual years, solid lines: trends in the whole period.

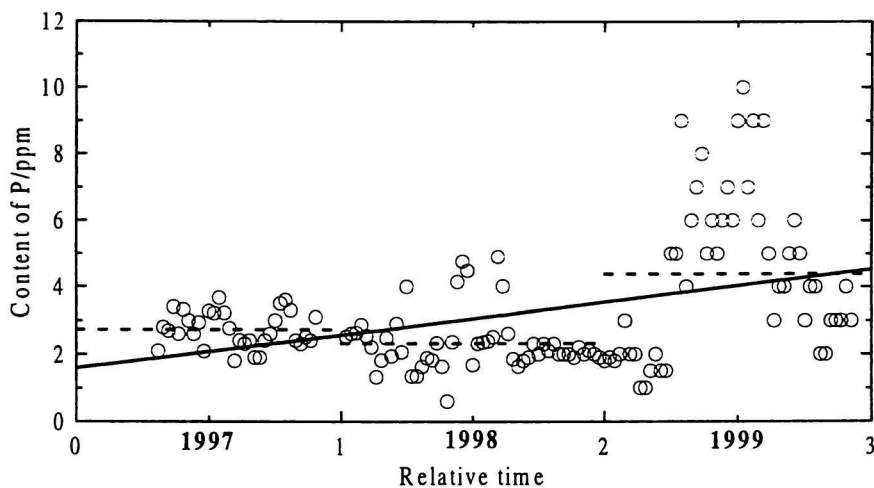


Fig. 5. Content of P in prebaked anodes in the period 1997—1999.

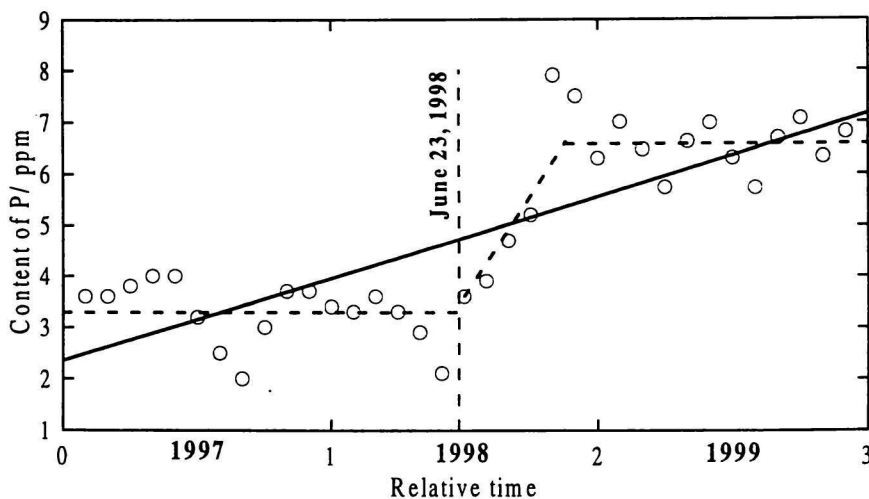


Fig. 6. Content of P in produced aluminium in the period 1997—1999.

PHOSPHORUS IN ALUMINIUM

Table 3. Consumed Amounts of Input Materials and the Calculation of Phosphorus Amount in Input Materials Related to the Production of 1 Ton of Aluminium in the Period 1997–1999

Material	<i>m</i> /kg	<i>w</i> (P ₂ O ₅)/%	<i>w</i> (P)/%	<i>m</i> (P)/g
Primary Al₂O₃				
1997:	1920	0.00086	0.00038	7.3
1998:	1920	0.00101	0.00044	8.5
1999:	1915	0.00083	0.00037	7.0
AlF₃				
1997:	17	0.0209	0.00920	1.6
1998:	15	0.0212	0.00933	1.4
1999:	13	0.0177	0.00779	1.0
Covering				
1997:	366	0.0077	0.0034	12.4
1998:	346	0.0152	0.0067	23.2
1999:	322	0.0103	0.0045	14.6
Anodes				
1997:	507		0.00051	2.6
1998:	553		0.00023	1.2
1999:	537		0.00044	2.4
Total P input				
1997:				23.8
1998:				34.3
1999:				25.0
Secondary Al₂O₃				
1997:	1920	0.0075	0.0033	63.4
1998:	1920	0.0060	0.0026	50.7
1999:	1925	0.0043	0.0019	36.4

P₂O₅ content in aluminium fluoride (Fig. 3). However, with regard to the low AlF₃ consumption this fact is not very important. The statistically important annual increase by 40 ppm is again given by the producer.

The average P₂O₅ content in fresh electrolyte was (90 ± 43) ppm (Fig. 4). The annual decrease by 43 ppm is not significant from the statistical point of view, however, it indicates a good trend. Substantially higher P₂O₅ content in the recycled electrolyte (Fig. 4), (215 ± 44) ppm, is due to the absorption of phosphorus in the crust near the anodes and smaller amounts are due to its introduction together with primary alumina and AlF₃ as anode covering. The annual decrease by 41 ppm is from the statistical point of view not significant, however it indicates again a good trend.

The average phosphorus content in prebaked anodes was (2.7 ± 0.5) ppm (Fig. 5). The annual decrease by 0.2 ppm is statistically nonsignificant.

The average content of phosphorus in metallic aluminium was (3.5 ± 0.6) ppm (Fig. 6). The statistically nonimportant decrease by 0.6 ppm, however, indicates again a favourable trend in the phosphorus balance in this year.

Providing the total phosphorus content in outgoing gases (56.1 g) is adsorbed in dry scrubbers, the

concentration of phosphorus in exhausting gases can be estimated. The total volume of exhausting gases is 95 455 m³ per 1000 kg of produced aluminium, from which it follows that the phosphorus concentration is 0.6 mg m⁻³. This value is very probable.

The total phosphorus material balance (inputs – outputs) in 1997 equals to –1.2 g P, which with regard to the statistical deviation in the individual average values, refers to the correctness of the phosphorus material balance.

Statistical Analysis of Phosphorus Content in 1998

The content of P₂O₅ in primary alumina in 1998 was (10.1 ± 1.3) ppm (Fig. 2). In this year only a statistically nonsignificant increase by 0.2 ppm may be observed, which was obviously caused by the producer.

For the total 1998 material balance the content of phosphorus in secondary alumina was not available. This value was thus estimated from the total trend in the period 1997–1999 as the mean value of the average content in 1997 and in 1999, i.e. 60 ppm P₂O₅. The total difference between the phosphorus amount in primary and secondary alumina per 1 ton of produced aluminium represents 42.2 g P. Again it was supposed that 95 % of this difference was adsorbed in

Table 4. Consumed Amounts of Output Materials and the Calculation of Phosphorus Amount in Output Materials Related to the Production of 1 Ton of Aluminium in the Period 1997–1999

Material	<i>m</i> /kg	<i>V</i> /m ³	<i>c</i> /(g m ⁻³)	<i>w</i> (P ₂ O ₅)/%	<i>w</i> (P)/%	<i>m</i> (P)/g
Aluminium						
1997:	1000				0.00035	3.5
1998:	1000				0.00043	4.3
1999:	1000				0.00065	6.5
Emissions						
1997:		95455	0.000029			2.8
1998:		96000	0.000022			2.1
1999:		96552	0.000015			1.5
Anode butts						
1997:	90				0.00027	0.2
1998:	116				0.00027	0.3
1999:	130				0.00027	0.4
Covering						
1997:	366			0.0097	0.0043	15.6
1998:	346			0.0176	0.0077	26.7
1999:	322			0.0119	0.0052	16.9
Total P output						
1997:					23.8	22.1
1998:					34.3	33.4
1999:					25.0	25.2
Input – output						
1997:						1.7
1998:						0.9
1999:						-0.2
Exhausting gases						
1997:		95455	0.00059			56.1
1998:		96000	0.00044			42.2
1999:		96552	0.00030			29.4

dry scrubber and 5 % escaped as emissions.

The average P₂O₅ content in aluminium fluoride, (212 ± 23) ppm (Fig. 3), is almost the same as in the previous year. The annual decrease by 25 ppm is again given by the producer.

The average P₂O₅ content in fresh electrolyte was (99 ± 67) ppm (Fig. 4). There is a statistically very significant annual increase by 156 ppm, which indicates some pot maintenance mistake. Substantially higher P₂O₅ content in the recycled electrolyte (275 ± 50) ppm (Fig. 4), is due to the absorption of phosphorus in the crust near the anodes and smaller amounts are due to its introduction together with primary alumina and AlF₃ as anode covering. The annual increase by 53 ppm is rather significant and indicates a not very favourable trend.

The average phosphorus content in prebaked anodes was (2.3 ± 0.9) ppm (Fig. 5). The annual decrease by 0.3 ppm is statistically not significant.

The average content of phosphorus in metallic aluminium was (4.3 ± 0.8) ppm (Fig. 6). The statistically very important increase by 4.4 ppm indicates again a nonfavourable trend in the phosphorus balance and

reflects some mistake in pot maintenance.

The total difference between the phosphorus content in input and output materials represents 1 g P. This small difference is within the statistical deviation in the average phosphorus content and refers again to the correctness of the phosphorus material balance.

Significant increase of phosphorus content in the middle of 1998 in produced aluminium as well as in the fresh and recycled electrolyte indicates some technological fault, most probably in the maintenance of the cells. Slight increase occurs also in the phosphorus content in prebaked anodes. It may be supposed that the reason for such behaviour was the temporal consumption in the cells of waste materials with a high content of phosphorus.

Statistical Analysis of Phosphorus Content in 1999

The content of P₂O₅ in primary alumina in 1998 was (8.3 ± 2.0) ppm (Fig. 2) with a statistically significant and favourable decrease by 3.9 ppm caused by the producer.

The average P_2O_5 content in secondary alumina was (43 ± 10) ppm (Fig. 2) with a nonsignificant annual increase by 3 ppm. The total difference between the phosphorus amount in primary and secondary alumina per 1 ton of produced aluminium represents 29.4 g P. Again it was supposed that 95 % of this difference was adsorbed in dry scrubber and 5 % escaped as emissions.

The average P_2O_5 content in aluminium fluoride, (177 ± 33) ppm (Fig. 3), is lower than in the previous year. The annual decrease by 91 ppm is again given by the producer.

The average P_2O_5 content in fresh electrolyte was (156 ± 32) ppm (Fig. 4). There is again a statistically significant annual increase by 34 ppm, which indicates again some technological fault, like the consumption in the cells of waste materials with a high content of phosphorus. Only a little higher P_2O_5 content in the recycled electrolyte (185 ± 28) ppm (Fig. 4), is most probably due to the successive mixing of both fresh and recycled electrolytes. The annual decrease by 20 ppm is not significant.

The average phosphorus content in prebaked anodes was (4.4 ± 2.4) ppm (Fig. 5). The annual increase by 2.0 ppm is statistically not significant.

The average content of phosphorus in metallic aluminium was (6.5 ± 0.5) ppm (Fig. 6). The statistically nonimportant increase by 0.2 ppm indicates again a nonfavourable trend in the phosphorus material balance.

The zero total difference between the phosphorus content in input and output materials refers again to the correctness of the phosphorus material balance.

CONCLUSION

From the results of the statistical analysis of phosphorus content in input and output materials used in Slovalco, a.s., Žiar nad Hronom, Slovakia, follows a steady increasing content of phosphorus in produced aluminium as well as in recycling materials in the period of 1997–1999, caused most probably by its accumulation in the cells.

The content of phosphorus in fresh electrolyte increased substantially in the middle of 1998 and in the end of 1999 becomes very close to the phosphorus content in recycled electrolyte. On the other hand, the content of phosphorus in the recycled electrolyte increased significantly in 1998 and culminated roughly in the middle of this year. In the end of 1999 it was very close to the content of phosphorus in the fresh electrolyte. The decrease of phosphorus content in the recycled electrolyte and its increase in the fresh one is obviously due to the successive mixing of both electrolytes.

The content of phosphorus in prebaked anodes substantially increased in 1999 to the average value of 4.4 ppm with a relatively large dispersion up to ± 5 ppm.

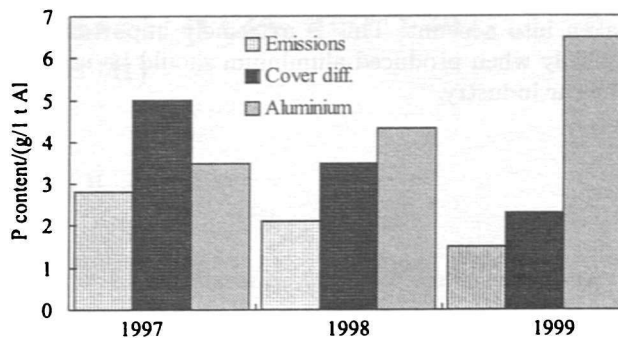


Fig. 7. Trends in the amount of phosphorus in produced aluminium, in emissions, and in the difference between the input and output anode covering in the period 1997–1999.

The reason for such increase is not clear yet, but it can be supposed that the reason may be in the successive accumulation of phosphorus in the whole process and therefore also in the recycled anode butts.

Interesting is the very significant decrease of the phosphorus content in secondary alumina. However, this observation is not necessarily important, since the analyses of phosphorus in secondary alumina were in 1997 performed only in a short time interval (three months) and in 1998 they were absent at all.

From the statistical point of view, the content of phosphorus in aluminium produced in the period 1997–1999 systematically increases with the average trend of $1.6 \text{ ppm year}^{-1}$. The substantial increase of the phosphorus content happened approximately in June 1998 (see Fig. 6). Similar effect has been observed also in the course of phosphorus level in fresh and recycled electrolytes (see Fig. 4).

Very important conclusion follows from the total phosphorus balance in the period 1997–1999 concerning the trends in the phosphorus mass flow. In Fig. 7 the amounts of phosphorus in produced aluminium, in emissions, and in the difference between the input and output covering are shown. The difference between the input and output covering refers to the amount of phosphorus absorbed in the covering during the electrolysis. From the figure it follows that while the amount of phosphorus in emissions and in the covering difference decreases, that in the produced aluminium increases. This means that practically all the introduced phosphorus gathers successively in the produced aluminium.

The significant increase of phosphorus content in the middle of 1998 in most of the followed materials indicates some technological fault. It may be supposed that the consumption in the cells of waste materials containing high levels of phosphorus was the reason of such behaviour. In order to prevent the further increase of phosphorus content in the produced aluminium some technological precaution should be

