Fizykochemiczne Problemy Mineralurgii, 24 (1991) 233-243

*Slawomir SOBIERAJ**
*John RALSTON**
*Roger St. C. SMART**

FLOTATION OF ZIRCON FROM MINERAL SANDS

Separation of zircon by flotation from two difference feeds derived from dry separation methods (i.e. ZrO_2 18.9%; 39.9%) has been tested for a variety of collectors and flotation conditions. Concentrates, with very low ThO_2 content (i.e. 0.02%) and acceptable grades (G) and recoveries (R) were obtained e.g. 51% ZrO_2 G, 80% R; 63% G, 80% R. Cleaning a final dry-separated zircon product using flotation also improved the grade by removal of Al_2O_3 and TiO_2. Part of the zircon, probably in metamict or surface-altered form, was difficult to float.

1. Introduction

Physical methods of concentration are most frequently used to separate minerals contained in alluvial or mineral sands deposits. There is now a substantial and growing interest in the use of flotation as an alternative beneficiation technique. From a purely economic point of view this process can be very effective, due to reduced costs involved in constructing and operating a smaller separation plant and in lower overall energy consumption. Furthermore, since all of the processes are run under wet conditions, radioactive dust problems can be effectively eliminated, since only the final concentrate requires drying.

The literature information on mineral sands flotation is sparse in comparison with the flotation of sulphides. Actual mechanisms of collector and depressant adsorption are very poorly understood. In most papers concerned with zircon flotation, attention has been focused on either oleic acid or sodium oleate as the collector, with sodium silicate as the depressant for gangue minerals [1-9]. Some authors used

*School of Chemical Technology, University of South Australia, The Levels. S.A. 5095 AUSTRALIA

soaps of saturated fatty acids as collectors [10,11]. From a survey of papers devoted to zircon separation from heavy mineral sands, the final concentrates contained no more than 90% of $ZrSiO_4$ (60% ZrO_2) and therefore found only limited application. In order to improve the quality of the zircon concentrate, a search for more selective collectors took place. Some reports from the Soviet Union demonstrate the potential use of aliphatic hydroxamates as selective collectors for zircon [12-15], but their industrial application seems to be limited due to the high cost of these reagents. In China [16] tolyl arsenic acid has been used in practice as a zircon collector, however its toxic properties make it impossible to use this reagent in Australia. In Taiwan [17] a combined flotation cycle (-rougher flotation at a pH of 8.4 with sodium oleate, followed by cleaning at pH 1.9 with sodium dodecylbenzenesulfonate) has been successfully tested, giving a concentrate with a grade of 98.7% $ZrSiO_4$ (66% of ZrO_2), but with a poor recovery of 62%. In recent times, reagents from a group of phosphonic acid derivatives have been investigated as collectors for zircon. Collins, Wright and Watson [18] indicate that Briquest product, alkyl imino-bis-methylene phosphonic acid sodium salts can efficiently float certain oxide and silicate minerals. The Hoechst Company also recommends reagents P-184 and P-195 (styrene and n-heptyl phosponic acids) for zircon flotation [19]. The aim of this research was to produce a high quality zircon concentrate of grade comparable or better than current commercial products produced by dry separation techniques. In this work we have focused our attention on a small group of commercial, readily available collectors and assessed their flotation performance.

2. Experimental procedure

2.1 Materials

a) Feed Materials

Three bulk sample of flotation feeds were used - Sample A, denoted "Zircon Circuit Concentrate" sample was generally used in the experimental programme. Some flotation tests have been carried out on Sample B, denoted "Zircon Concentrate" in order to determine the possibility of quality improvement of actual commercial grade zircon product. Preliminary investigations have also been carried out on Sample C, denoted "Leucoxene Circuit". Feed assays of the samples are shown in the Table 1.

Tab. 1.
Feed assays

Name	Fe_2O_3 %	TiO_2 %	P_2O_5 %	Al_2O_3 %	ZrO_2 %	SiO_2 %	ThO_2 %
1. Zircon Concentrate	0.08	0.15	0.08	0.75	64.06	32.61	0.01
2. Zircon Circuit Conc.	4.15	20.42	1.19	1.82	39.90	24.61	0.30
3. Leucoxene Circuit	10.19	43.61	0.42	3.35	18.87	17.49	0.11

b) Reagents Tested

Details of the collectors and depressants used in this testwork are shown in Table 2. They were obtained from technical grade materials. The pH of the slurries was adjusted using sulphuric acid or sodium carbonate. Flotation experiments were conducted using deionized water. The amount of collector stipulated in particular flotation runs is quoted for the pure substance except for the Briquest reagents which are delivered in the form of a solution, with the concentration of active substance at 25% by weight.

Tab. 2.
Collectors and depressants

1. Briquest 281 - 25S	[2-Ethylhexyl-N-$(CH_2PO_3Na_2)_2$]
2. Briquest 2N81 -25S	[n-Octyl-N-$(CH_2PO_3Na_2)_2$]
3. Briquest 291 - 25S	[iso-Nonyl-N-$(CH_2PO_3Na_2)_2$]
4. Briquest 2121-25S	[Dodecyl-N-$(CH_2PO_3Na_2)_2$]
5. Hoechst - P-184	Styrene Phosphonic Acid
6. Hoechst - P-195	n Hexyl Phosphonic Acid
7. Sodium silicate	Na_2SiO_3
8. Sodium dithionite	$Na_2S_2O_4$

c) Flotation Procedures

Flotation experiments were performed in a self-aerated flotation machine with a cell volume of 1.0 litre. The pulp density was 30%, whilst the conditioning time with a depressant was 10 minutes and 5 minutes with a collector. Flotation tests were carried out using staged collector addition. In all flotation experiments, Aero 65 was used as the frother at a concentration of 0.02 kg/T. In some cases, when high collector consumption was required, kerosene was applied as a froth destabilizer.

3. Analitical

All analyses associated with this testwork were conducted using the XRF technique.

4. Results

The flotation results are presented in the form of both a Table as well as grade/recovery or grade/yield curves for zircon dioxide and other oxides. The detailed conditions under which each flotation test were carried out are described in the full set of results for each of the flotation runs.

4.1. Flotation results for Sample A, "Zircon Circuit Concentrate" feed.

This feed, as can be seen from the chemical assay (Table 1), represents a mixture of heavy sand minerals after WHIMS ilmenite separation. In comparison with Sample B it has a much higher slime content and needs to be carefully deslimed before flotation. In five desilming steps sodium silicate was used in a total amount of 0.5 kg/T at a pH of about 10 for effective slime dispersion.

Flotation tests were performed in order to test the possibility of producing high zircon grade concentrates using this procedure. The results for zircon are shown in Figures 1-5, and for thorium in Figures 6 and 7.

4.1.1. Flotation with Briquest collectors.

Flotation results for Briquest 2N81 are shown in Figure 1. It can been seen that flotation is very pH sensitive. The necessary amount of collector (the collector consumption is shown in the brackets) varies from 0.3 kg/T at pH 5 to 4.4 kg/T at pH 2. The selectivity of flotation also depends on pH; the lower the pH the better the results. The best concentrate grade (62% ZrO_2 with recovery 77%) was obtained at pH 2, but with a high consumption of collector. Comparison of the results leads to the conclusion that the flotation circuit should operate at pH 4-5 in the scavenger bank, pH 3-4 in rougher flotation step and pH 2-3 in a cleaner. This procedure will permit reduced collector consumption and increased grade and recovery. Additional grade improvement can be obtained using a suitable depressant for the gangue minerals.

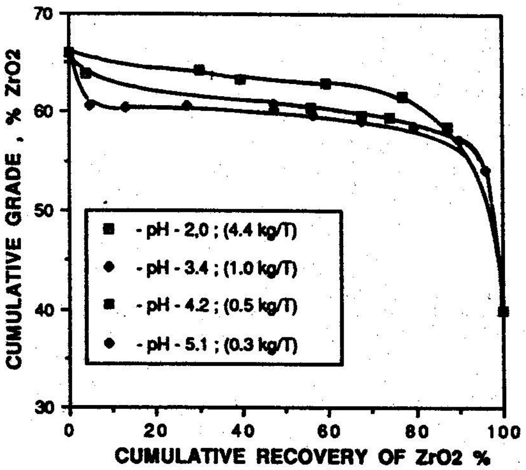

Fig.1.
Grade vs recovery curves for Briquest 2N-81 collector

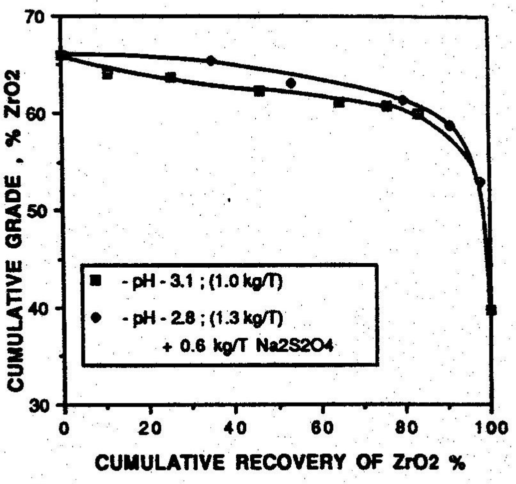

Fig.2.
Grade vs recovery curves for Briquest 281 collector

<u>The best flotation results in this report were obtained with Briquest 281 (ethylhexyl radical) and are presented in Figure 2</u>. As can be seen from the data, flotation at pH 3-3.3 gave a concentrate with a grade of 60% ZrO_2 and a high recovery of 84%. A significant improvement is achieved when sodium dithionite is used as a depressant under similar conditions. It is possible then to reach almost 62% ZrO_2 grade with a recovery of 80%, or 60% ZrO_2 grade with a recovery of 90%, in a single flotation step.

Figure 3 illustrates some of the results from tests in which Briquest 291 was used as the collector. This reagent, which has a slightly longer hydrocarbon chain than tested previously (nonyl instead of octyl) showed similar flotation behaviour (grade and recovery as well as collector consumption are very pH sensitive) but, in general, the selectivity was poorer. It is possible to use Briquest 291 in the scavenger flotation bank (note there is still very good selectivity against P_2O_5 and Al_2O_3) because it has higher collection power then Briquest 2N81 at the some concentration.

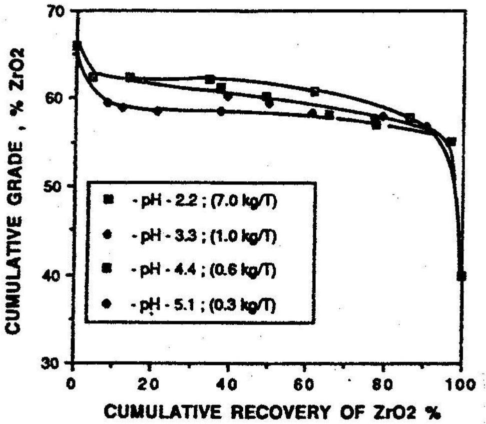

Fig. 3.
Grade vs recovery curves for Briquest 281 collector

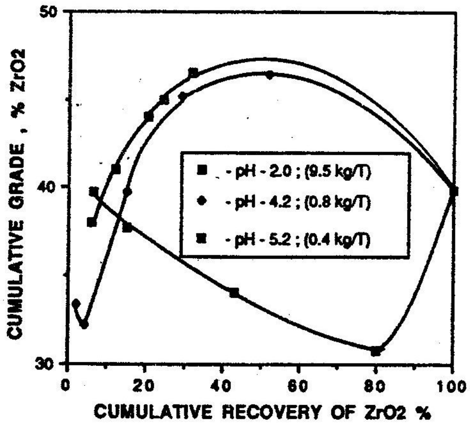

Fig. 4.
Grade vs recovery curves for Briquest 2121 collector

The results for Briquest 2121 (dodecyl) are presented in Figure 4. As can be clearly seen, very poor selectivity is found across the pH range from 2-5, due to a high level of quartz flotation with this reagent. The lost of selectivity against titanium minerals and aluminosilicates is also evident. In some cases the content of ZrO_2 in concentrates is lower than in the feed. It indicates that this collector is inappropriate for zircon flotation from that particular feed.

4.1.2. Flotation with Hoechst collectors.

These flotation tests were carried out with P-184 and P-195 collectors, which were strongly recommended as being selective for oxide and silicate minerals in the literature. The results for P-184 and P-195 are shown in Figure 5. The P-184 collector, in a similar fashion to the Briquest reagents gave a better selectivity at lower pH but its consumption was higher (0.8 kg/T P-184 in comparison with 0.25 kg/T B-281 of pure active substances). The best single zircon concentrate in this work, containing 65.5% of ZrO_2 was obtained with this reagent-note that the pure zircon mineral from the tested feed contains 66% of ZrO_2. The combined zircon concentrates from this test gave a final product with a high grade of 63% ZrO_2, however the recovery was slightly lower than that obtained for some of the Briquest reagents.

Collector P-195 showed a very high flotation activity for all of the feed's components at very low concentration (0.15 kg/T) and therefore has not been tested further.

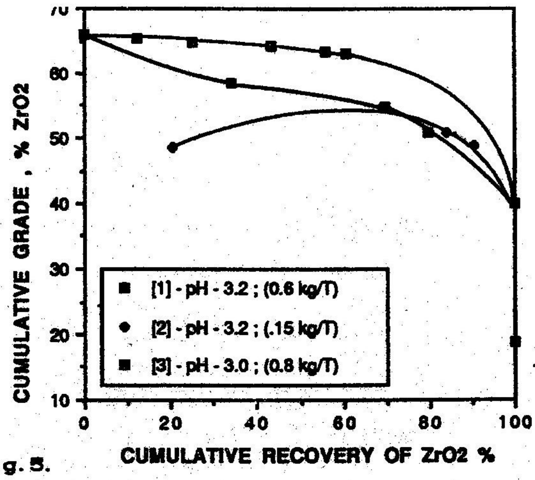

Fig. 5.

Grade vs recovery curves for Hoechst collectors. [1,3]-P-184; [2]-P-195. Curve [3]-leucoxene circuit feed

One preliminary flotation test was conducted on a sample of Leucoxene circuit with collector P-185. This feed contains a relatively lower concentration of zircon and a higher amount of titanium minerals. The results are also presented in Figure 5. From a feed of about 17% ZrO_2, a final concentrate was obtained with a grade of 51% ZrO_2 and a recovery of 80% in one flotation step. The recoveries of other oxides in this concentrate are still very low in comparison with zircon (7% TiO_2, 5% P_2O_5 and 13% Al_2O_3).

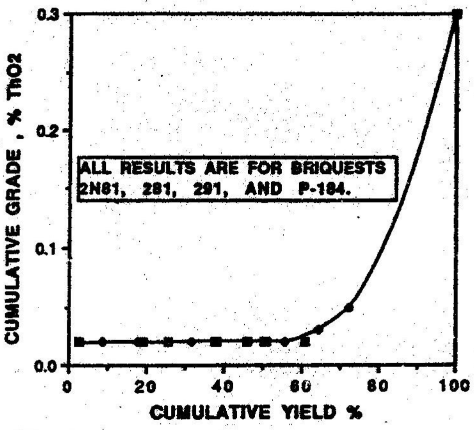

Fig. 6.

The relationship between cumulative grade of ThO_2 and cumulative yield of concentrates

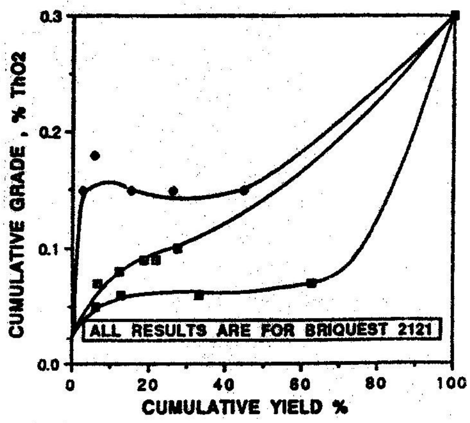

Fig. 7.

The relationship between cumulative grade of ThO_2 and cumulative yield of concentrates

In Figures 6 and 7 the relationship between cumulative grade of thorium oxide and cumulative yield of concentrates are presented. The selectivity of separation against ThO_2 is very high for Briquests 2N81, 281, 291 and Hoechst P-184. All experimental points lay on the same curve, which possesses the ideal separation shape. These results show that is possible to produce final zircon concentrates with a very low content of ThO_2 (0.02% from the feed value of 0.30%). In the case when Briquest 2121 was used as collector the selectivity against thorium is evidently lower (Fig. 7).

4.2. Flotation results for Sample B, "Zircon Concentrate" feed.

These experiments were carried out in order to determine the possibility of quality improvement of the final zircon concentrate following the dry separation plant. The results are presented in Table 3. It can be clearly seen that it is possible to remove some of the contaminants, especially aluminosilicates and titanium minerals, which reduce the overall quality of the present product. It is feasible to reduce the Al_2O_3 content in the zircon concentrate to level of 0.20% from the feed, which contains 0.75% of this compound, as well as to decrease the TiO_2 content from 0.15% to 0.08%. However, the content of P_2O_5, ThO_2 and Fe_2O_3 remains constant in all of the flotation products.

Tab. 3.

Flotation results for "Zircon Concentrate" feed

	ZrO_2		Al_2O_3		TiO_2		Fe_2O_3		P_2O_5	
	Ass. %	Rec. %	Ass. %	Rec. %	Ass. %	Rec. %	Ass. %	Rec. %	Ass. %	Rec. %
1	64.8	73.1	0.17	19.7	0.08	31.1	0.07	49.8	0.07	69.2
2	64.6	73.2	0.18	21.2	0.08	37.1	0.07	63.5	0.08	71.9
3	64.8	78.5	0.27	47.9	0.08	21.9	0.07	61.8	0.08	74.0
Feed	64.1		0.75		0.15		0.08		0.08	

Conditions:

1. Depressant Na_2SiO_3 - 0.25 kg/T
   Collector Briq. 291 - 0.25 kg/T
   pH - 3.0 ÷ 3.6
2. Depressant Na_2SiO_3 - 0.25 kg/T
   Collector Briq. 2N - 81 - 0.6 kg/T
   pH - 3.5 ÷ 4.0
3. Depressant Na_2SiO_3 - 0.25 kg/T, $Na_2S_2O_4$ - 0.6 kg/T
   Collector Briq. 291 - 1.2 kg/T
   pH - 3.2 ÷ 3.6

5. Summary

1. Flotation tests have been conducted on samples of zircon bearing feeds from a dry separation mill. The testing was aimed at identifying suitable collectors and flotation conditions to produce a high grade zircon concentrate.
2. Flotation tests showed that the most selective collectors for this purpose are Briquest 2N81 and 281 and Hoechst P-184, used at low pH.
3. It has been shown that it is possible to significantly improve the quality of the final "commercial" grade zircon concentrate using flotation as an "additional cleaning" step operation.
4. It has been shown that it is possible to produce a high grade zircon concentrate with a very low ThO_2 content and with acceptable recoveries from the preliminary products of separation in a dry mill.
5. To increase the recovery of zircon concentrate, more work must be done in order to explain the difficulties in flotation of a part of the zircon. A part of zircon as probably in the form of metamict or structurally altered zircon which has different flotation properties to the main zircon fraction. This will require careful further study.

6. References

1. Abdel Rehim, A., Beneficiation of Low Grade Zircon Concentrate", J. Inst. Eng. (India) Part MM, 58(3), 99-102, 1976.
2. Cabezas, J.L., Mato, F., Sastre, H., Flotation Recovery of Zircon and Rutile from a Uraniferous Quartzite, Rev. Metal. (Madrid), 22 (2), 102-107, 1986.
3. Dixit, S.G., Biswas, A.K., pH-Dependence of the Flotation and Adsorption Properties of Some Beach Sand Minerals, Trans. AIME, 244 (2), 173-178, 1969.
4. Dixit, S.G., Biswas, A.K., Solid-Liquid Interfacial Parameters in Zircon-Sodium Oleate Moderator Flotation Systems., Trans. Indian Inst. Met., 29(1), 23-29, 1976.
5. Dixit, S.G., Biswas, A.K., Zircon-Sodium Oleate Flotation System. 1. Solid-Liqud Interfacial Parameters, Trans. Inst. Min. Metall., (Sect. C), 82 (Sept), C140-C144, 1973.
6. Dixit, S.G., Biswas, A.K., Zircon-Sodium Oleate Flotation System. 2. pH Dependence of Collector Adsorption and Critical Contact Phenomena, Trans. Inst. Min. Metall., (Sect. C), 82 (Dec), C202-C206, 1973.
7. Bebesh, A.A., Effect of Regulator Reagents on Mineral Flotation During Aerosol Treatment, Obogashch. Polez. Iskop., Respub. Mezhvedom. Nauch.-Tekh. Sb., 58-61. From: Ref. Zh., Met.1972, Abstr. No.

4G144.

8. Zakharova, I.B., Morozov, G.G., Flotation Properities of Zirconium Minerals, Obogashch. Rud. (Irkutsk), 50-59, 1982.

9. Terets, G. Ya., Krichenko, T.F., Shapovalóv, G.M., Effect of Sodium Phosphates on the Flotation of Monazite, Zircon, Ilmenite, and Attendant Minerals by Sodium Oleate, Fiz-Khim. Osn. Kompleks. Pererab. Rud Sredniei Azii, 226-229, 1970

10. Zadorozhnyj, V.G., Safronov, A.F., Ter-Daniel'yants, K.R., Bukhvalov, N.P., Tischenko, A.G., Kopaev, A.A., Results of Industrial Tests of Acid Still Residues for Flotation of Sands from Titanium-Zirconium Placer Deposits, Tsvetn. Met., 40(7), 23-26, 1967.

11. Luszczkiewicz A., Flotation of Zircon from Byproducts of Sand Beneficiation, Fizykochem. Probl. Mineralurgii, 16 (Mater. Symp. Doskonalenie Procesow Przerobki Surowcow Mineralnych.), 63-70, 1984.

12. Naifonov, T.B., Mikhailuk, B.Z., Zakharova., I.B., Morozov, G.G., Klyuchnikova A.M., Mechanism of the Effect of Hydroxamic Acids in Flotation Titanium and Zirconium Minerals, Flotatsionnye Reagenty, 110-115. Edited by Gol'man A.M., Dimitrieva, I.L., Nauka: Moscow, USSR, 1986.

13. Polkin S.I., Adjamov E.V., Pai K.M., Linnik O.B., Flotation of Beach Placer Minerals vy the Complexing Reagent IM-50, Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall., 17(5), 3-10, 1974.

14. Naifonov T.B., Mikhailyuk B.Z., Zakharova I.B., Morezov G.G., Klyuchnikova A.M., Mechanism of the Effect of Hydroxamic Acids in Flotation of Titanium and Zirconium Minerals and Ores, Flotatsionnye Reagenty, 110-116, Edited by: Golman, A.M., Dimitrieva I.L., Nauka: Moscow, USSR, 1986.

15. Tiunov A.A., Maslovskaya I.Yu., Gorokhov N.P., Pilot Test of Flotation of Columbite and Zircon by Hydroxamic Acids, Tsvetn. Met. (Moscow), (4), 103-104, 1989.

16. He J.Z., Liu M.X., Innovation in Separation Technology for Fine Gravity Semiproducts, Report, ISTIC-TR-C-00157, Order.No. PB89-112478, 13 pp. Avail. NTIS From: Gov. Rep. Announce. Index (U.S.) 1989, 89 (2), Abstr. No. 904,379.

17. Lee, Ming-I., Lee, Cheng-Yi., Kao, Chih-Chun., Benefication of Zircon By Flotation, K'uang Yeh Chi Shu, 16(7), 365-375, 1978.

18. Collins D.N., Wright R., Watson D., Use of Alkyl Imino-bis-methylene Phosphonic Acids as Collector for Oxide and Salt-Type Minerals, Reagents in Miner., Ind. Paper 1-12, Edited by: Jones M.J., Oblatt R., Inst. Min Metall: London, U.K., 1984.

19. Mining Chemicals Handbook, Copyright by the Hoechst Company.

Streszczenie

Sobieraj S., Ralston J., Smart R. St.C., 1991, Flotacja cyrkonu z piasków mineralnych. Fizykochemiczne Problemy Mineralurgii, 24, 233-243. (English)

Wydzielanie cyrkonu metodą flotacji z dwóch różnych nadaw otrzymanych na drodze suchej separacji (o zawartości ZrO_2 odpowiednio 18.9% i 39.9%) było badane przy użyciu kilku zbieraczy i w różnych warunkach. Otrzymano koncentraty o niskiej zawartości ThO_2 (0.02%) przy zadowalającej jakości (G) i Uzysku (R) (odpowiednio G: 57% i 63%, R: 80%). Wykazano również, że możliwe jest poprawienie jakości finalnego, obecnie produkowanego koncentratu cyrkonu w jednym z zakładów w Australii na drodze flotacji. Część cyrkonu, występująca prawdopodobnie w postaci zmetamiktyzowanej bądź powierzchniowo przeobrażonej nie ulega flotacji.