TECHNOLOGIES FOR EXTRACTION OF COPPER FROM COPPER SLAG BY FLOTATION

Turakhodjaev Nodir, Tashbulatov Sherzod, Chorshanbiev Shukhrat
Tashkent State Technical University, Uzbekistan
Email: t.sh.b.zohid@mail.ru

Abstract - The technology of flotation processing of slags of the Copper Plant, both stored in the slag dump and generated in the course of its current activity, has been proposed. Variants of autonomous processing of slags of various types, as well as their mixtures in different proportions, are considered. The technology development was based on a deep study of the material composition of slags. The results of X-ray microprobe studies of slag samples showed that the main mineral phases that make up their composition are magnetite and various silicates. The laboratory studies of fractivity and grindability have shown that dump slags, in accordance with the accepted classification, are difficult to crush and difficult to grind. Based on the results obtained, an option was selected that provides for two stages of medium crushing in cone crushers and one stage for fine crushing in a high-pressure roller crusher. Further grinding occurs in two stages with obtaining a product containing 70% of the control class of size –0.045 mm, and the material is fed to flotation.

Keywords: Technological process, Mathematical model, Moisture content, Copper extraction, Slag processing, Melting furnace, Flotation processing.

1. Introduction

The object of the research is the developed technology for extracting copper from industrial slags by flotation. Most of the world's copper production is produced by smelting flotation copper sulphide concentrates in reverberatory furnaces, followed by oxidation of matte to blister copper in a converter. The slag from the converter contains too much copper to be sent to landfill and is returned to the reverberatory furnace to recover most of the copper.

This method of removing the converter slag, although simple, complicates the operation of the reverberatory furnace and significantly contributes to the loss of copper in the reflective slag. An economical method for separate processing of converter slag would increase the productivity of the furnace, produce lower quality slag and simplify the operation of the furnace.

Table 1. Chemical analyses of converter slags

Slag	Analyses, percent								
	Cu	Fe	S	Zn	SiO_2	Al_2O_3	MgO	CaO	Fe_3O_4
A	0.6	49.1	0.8	0.3	26.8	1.3	1.0	0.2	53.1
B	2.0	46.4	1.5	-	27.4	0.6	0.9	0.4	39.2
C	2.6	48.3	2.6	0.4	20.4	1.0	0.9	0.5	51.8

Opportunities to minimize copper losses in converter slags include:

(1) settling the molten slag to recover entrained matte and copper,

(2) smelting slag with a suitable reducing agent to recover copper-iron alloy or low grade matte

(3) enrichment of slags by magnetic separation

(4) treatment of slag by flotation. Flotation appears to be the most promising for the economical recovery of copper.

The Mining Bureau conducted flotation and grindability tests on three converter slags containing 1.6 to 6.6 percent copper. The relative advantages and costs of flotation of slowly cooled and water cooled slags were determined.

2. Description of Slag Samples

Three BOF slag samples used in the study were obtained from a western smelter slag Sample A, which contained 0.6 percent copper, was a 5 ton composition of four defatted slags taken over a typical 14 hour processing cycle. A portion of each defatted mass was poured into a defatting ladle and the mass was allowed to cool slowly for 31 hours before discarding and crushing.

Sample B, containing 2.0 percent copper, was 1 ton of converter slag. Neither the thermal history nor the defatted layer from which the sample was obtained was known.

Sample C, which weighed about 0.5 tonnes, was not a typical sample as the 2.6 percent copper content was higher than the 1 to 5 percent copper reported for most BOF slags. However, operational changes sometimes result in unusually high copper slag contents. This sample was included in the study, as the reprocessing process would have to process all types and grades of converter slag. Again, the thermal history was not known, but it was assumed that the slag was slowly cooling.

The study of slag samples using electron microprobe and metallographic microscope showed that copper is contained mainly in the form of copper sulfide, approximately corresponding to the composition of bornite. Most of the sulfide particles ranged in size from 10 to 45 microns. Some sulphides occurred as stringers, but most were present as rounded particles. Magnetite was observed both as dendrites and well-formed crystals. Several sulfide inclusions were observed in magnetite. The forms of copper in these slags agree with the conclusions of other researchers about the presence of copper slag from smelting furnaces. A photomicrograph of a typical slag is shown in Figure 1.

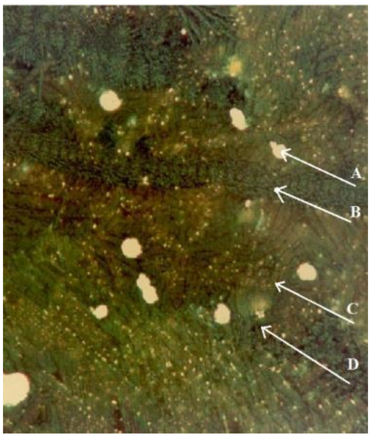

Figure 1: Typical Converter Slag(x400). A.Copper sulfide, rounded white areas; B.magnetite, very light gray; C.crystalline phase of siliceous partion, light gray; and D, noncrystalline phase, darker gray

3. Slag Sample Preparation

Slag samples were prepared for enrichment and grinding studies by remelting 1 kg charges in an induction furnace. The samples were then cooled by pouring them into a water bath to cool the slag, cooling the crucible and melting in air or slowly cooling in a furnace.

The water quenched slag solidified into granules, most of which were minus 6 mesh. Air-cooled and slowly cooled slags solidified in the form of separate masses. Cooling curves were obtained by immersing a chromel-alumel thermocouple with quartz protection into the charge while recording temperatures on a strip recorder. The cooling rates of samples with slow cooling and air cooling in an induction furnace are shown in Figure 2.

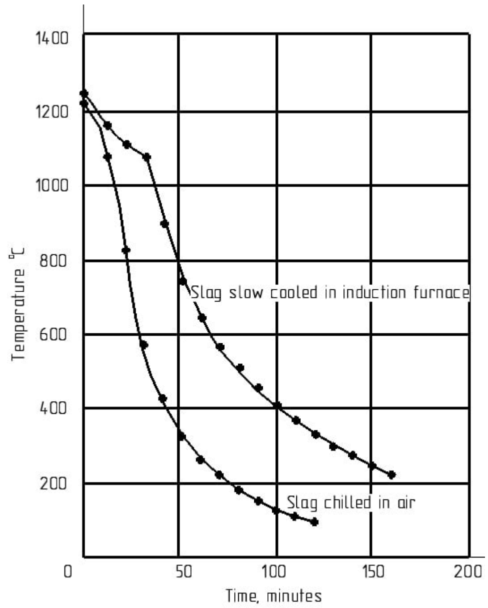

Figure 2: Cooling Rates of Slag Chilled in Air and Slow Cooled in the Induction Furnace

The quenched slags used in the grindability tests were dry ground to minus 6 mesh, while the slags used in the flotation tests were ground to minus 10 mesh. The slowly cooled slag was similarly ground after breaking up and separating the refractory clay crucible from the solidified slag.

Samples of heat-treated slags were polished and examined under a microscope. In the samples quenched with water, the bulk of copper was present in the form of round inclusions, which had a light blue color, characteristic of chalcocite. Particle sizes ranged from 10 mesh to about 15 microns. Many of the larger chalcocyte inclusions contained metallic copper stringers. In addition to chalcocyte, finer particles exhibiting the color and characteristics of bornite were observed in the minus 15 micron range. The extremely fine particle size of these particles indicated that micronization would not significantly improve copper recovery. Copper recovery was only slightly higher with 60 minutes grinding than with 10 minutes grinding.

The slowly cooled slags were similar in appearance to slags obtained from a smelter. Both sulfide inclusions and magnetite crystals were more angular than those observed in water-quenched samples.

4. Methods

The ability of various slags to concentrate by flotation was determined using the following procedure. Standard 500 gram charges of dry ground slag were wet milled at 62.5% solids in an iron ball mill, wet sieved to remove any metal particles larger than 65 mesh and to determine the pH of the slurry. The charges were milled for 10, 30, and in some cases 60 minutes to ensure optimal release of copper minerals.

Batch flotation tests were carried out on ground cellulose in a 600 gram Fagergren-type chamber. Three successive coarser concentrates were initially recovered.

Before each 3 minute flotation period, the slags were conditioned for 5 minutes with 0.1 lb / ton of potassium amylxanthate collector (KAX) and 0.18 lb / ton of methyl isobutyl carbinol blowing agent (MIBC). Since virtually all of the recoverable copper was found in the first two roughnesses, the third roughness was removed during subsequent flotation tests. Refinement tests for coarser concentrates were not tested in these batch tests.

- ***Copper Flotation From Slow Cooled Converter Slag***

The results of flotation tests on slags cooled in air and in an induction furnace are shown in Table 2-3.

Table 2. Grinding and flotation data for slags cooled in air

Grinding			Flotation		
Slag	Time, min	Distribution, size	Product	Analysis, pct Cu	Distribution, pct Cu
A	10	94 pct minus 325 mesh.	Concentrate Tailings	8.9 0.41	81.0 19.0
A	30	84 pct minus 100 mesh.	Concentrate Tailings	10.1 0.30	86.5 13.5
B	10	90 pct minus 325 mesh.	Concentrate Tailings	35.1 0.63	88.4 11.6
B	30	82 pct minus 100 mesh.	Concentrate Tailings	25.5 0.37	93.4 6.6
C	10	94 pct minus 325 mesh.	Concentrate Tailings	30.2 0.46	94.5 5.5
C	30	84 pct minus 100 mesh.	Concentrate Tailings	28.7 0.36	95.6 4.4

5. Research Results and Discussion

Examination of the data shows that relatively fine grinding is required to release the trapped metal particles. After 30 minutes of grinding, 98 percent of the pulp passed through the 200 mesh. More than 80 percent were thinner than 325 mesh. The analysis and distribution of copper in the tailings obtained at 30 and 60 minutes grinding, as shown in Table 3, showed no advantage with grinding times exceeding 30 minutes. However, the analysis of copper in the tailings was lower and there covery of concentrates was markedly increased with 30 minutes grinding compared to 10 minutes grinding, as shown in the tables. Comparison of the two tables shows no significant difference in the results obtained when the slags are cooled in air or in an induction furnace.

The recovery of copper in concentrates from slag cooled in an induction furnace and crushed for 30 minutes ranged from 87.1 to 96.2 percent, with the best recovery obtained on a sample of premium slag. The copper content in the flotation tailings, which is the most important indicator, ranged from 0.26 to 0.39 percent. Coarser flotation data for individual products from slags, slowly cooled in an induction furnace and milled for 30 minutes, are shown in Table 4. Similar patterns of copper recovery were obtained during flotation tests carried out on slags prepared at different cooling rates and grinding times.

- ***Copper flotation from water hardened converter slag***

The test procedure used in the flotation of copper from induction furnace slag and water quenched was identical to that for slowly cooled slag. Visual observation did not reveal significant differences in flotation performance.

All slag pulps had a pH of about 8.5 and had a strong foam in the first coarser concentrate. There were some color differences in the slags. The water-hardened slags were black, while the slowly cooled slags were dark gray.

The results of flotation tests after water quenching of the three slags are shown in Table 5. Higher quality concentrates were obtained from water quenched slags than from slowly cooled slags, as shown by comparing the results shown in Table 5 with those listed in Tables 2-3. However, copper recovery was about 4 percent lower for the high copper content slag (Sample C) and 23 percent lower for the low copper content slag (Sample A). The hardened slag flotation tailings ranged from 0.53 to 0.66 percent; slowly cooled slags produced tailings containing as little as 0.26 to 0.39 percent copper, with the lowest assays at 30 minutes.

Table 3. Grinding and flotation data for slags cooled in the induction furnace

Grinding			Flotation		
Slag	**Time,min**	**Distribution, size**	**Product**	**Analysis, pct Cu**	**Distribution, pct Cu**
A	10	93 pct minus 100 mesh.	Concentrate Tailings	11.1 0.39	81.8 18.2
A	30	98 pct minus 200 mesh 84 pct minus 325 mesh	Concentrate Tailings	10.3 0.26	87.1 12.9
A	60	25 pct minus 20 microns.		11.4 0.18	
B	10	92 pct minus 100 mesh.	Concentrate Tailings	22.2 0.39	92.9 8.5
B	30	98 pct minus 200 mesh. 82 pct minus 325 mesh	Concentrate Tailings	27.5 0.39	91.8 8.2
B	60	86 pct minus 200 mesh 17 pct minus 20 microns	Concentrate Tailings	27.3 0.39	95.0 5.0
C	10	94 pct minus 100 mesh.	Concentrate Tailings	26.4 0.42	93.6 6.4
C	30	99 pct minus 200 mesh. 84 pct minus 325 mesh.	Concentrate Tailings	28.3 0.31	94.5 5.5 96.2 3.8
C	60	16 pct minus 20 microns.	Concentrate Tailings	25.4 0.40	95.9 4.1

Comparison of the size distribution of the flotation feed given in Tables 2-3 and 5 shows that for equal grinding times, the water hardened slags were coarser and more difficult to grind.

Table 4. Rougher flotation data for slag's slow cooled in the induction furnace and ground 30 minutes

Slag	Product	Analysis, pct Cu	Distribution, pct Cu
A	Plus 65-msh prills	20.4	0.2
	Rougher concentrate No. 1	16.1	82.9
	Rougher concentrate No. 2	1.7	4.0
	Rougher concentrate No. 3	0.7	1.5
	Rougher tailings	0.24	11.4
B	Plus 65-msh prills	32.1	0.3
	Rougher concentrate No. 1	42.6	73.9
	Rougher concentrate No. 2	12.2	20.8
	Rougher concentrate No. 3	0.7	0.9
	Rougher tailings	0.29	4.1
C	Plus 65-msh prills	56.1	0.5
	Rougher concentrate No. 1	46.0	83.2
	Rougher concentrate No. 2	7.9	12.5
	Rougher concentrate No. 3	1.1	1.5
	Rougher tailings	0.21	2.3

Table 5. Grinding and flotation data for water-quenched slags

Grinding			Flotation		
Slag	Time, min	Distribution, size	Product	Analysis, pct Cu	Distribution, pct Cu
A	30		Concentrate Tailings	17.0 0.53	70.7 29.3
B	10	81 pct minus 100 mesh 56 pct minus 150 mesh	Concentrate Tailings	28.6 0.62	88.4 11.6
B	30	97 pct minus 200 mesh 80 pct minus 325 mesh	Concentrate Tailings	38.8 0.54	89.3 10.7
C	10	80 pct minus 000 mesh 54 pct minus 150 mesh	Concentrate Tailings	33.8 0.80	90.4 9.6
C	30	97 pct minus 200 mesh 78 pct minus 325 mesh	Concentrate Tailings	32.5 0.66	91.6 3.4

This indication has been confirmed in subsequent grindability tests.

The tailings of both slowly cooled and water-cooled slags were examined under a microscope. Virtually all of the individual free copper-copper sulfide particles were recovered from the slag. The few remaining particles of copper sulphide were blocked by slag.

- ***Grindability definition***

In preparation for flotation, the molten converter slag can be either water-cooled or slowly cooled. The cooling method used in commercial operation will depend on the buoyancy of the copper from the water-quenched slag versus slow cooling, the initial and operational cost of the plant required to quench or slowly cool the slag, and the ability to grind the corresponding slag. Grindability was determined using a standard laboratory Bond ball grindability test.

Grinding bond theory (1) is widely recognized as a method for predicting labor costs in commercial crushing and grinding operations. Ball mill grindability tests calculate performance values (2) and these values serve as a basis for comparing grindability of different materials.

Numerically, the working index is the kilowatt-hours per short tonne required to reduce material from a theoretically infinite feed rate to 80 percent passing through 100 microns. This comminution parameter expresses the resistance of the material to crushing and comminution.

The laboratory ball mill test procedure simulates a closed loop dry grinding operation using a 250 percent circulating load at the specified screen size used in the test. For convenience, 65 mesh was selected as the throughput for the ball mill test in this study, as smaller sizes provide less reliable estimates of performance. Performance based on 80 percent of 100 micron transmission was calculated using coupling equations based on data collected during testing.

The work indexes determined for each of the heat-treated converter slag samples are shown in Table 6. The table also shows the work index definitions made on slag samples A and B obtained from the smelter. Examination of the data shows that water quenching makes slag grinding more difficult than slower cooled slags. The average working index for hardened slags was 18.1. Averages of 15.6 and 14.7 were recorded for slag air cooled and slowly cooled in an induction furnace.

Table 6. Work indices of converter slags for different cooling rates

Heat treatment	Work index			
	A	B	C	Average
Remelted in the induction furnace and water quenched	19.1	17.7	17.6	18.1
Remelted in the induction furnace and chilled in air	14.8	16.5	15.5	15.6
Remelted and cooled in the induction furnace	14.5	15.9	13.9	14.7
As received from the smelter	13.2	16.0	-	-

For comparative purposes, grindability tests were also carried out on two porphyry copper ore samples and a limestone sample.

The performance values determined for these materials were 10.6, 15.4 and 11.6. From these data, it follows that grinding the slowly cooled slag requires more energy than grinding conventional porphyry copper ore.

- ***Method for producing slowly cooled slag***

Slag from the copper converter is removed into ladles, which are lifted onto a tipping machine. Slag is poured into 10 x 32 x 4 ½ "molds mounted on a 430 ft long chute conveyor. Each mold is divided into three sections that produce 10 "by 10" by 4 1/2 "slag ingots. Conveyor speed of 7 feet per minute provides cooling from 1300 ° to 300 ° C. in about 1 hour. The solidified slag is discharged into an overvoltage storage hopper.

The crushing plant operates 7 days a week on a day shift only. With a capacity of 1,000 tons per day, slag ingots are crushed from 10 to minus ½ inch in two stages. In the first stage, the slag is crushed to minus 2 and a half inches in a 36 "by 42" ton crusher; The 5 and a half foot short head cone crusher further reduces slag to minus ½ in. A ½ "vibrating screen installed upstream of the secondary cone crusher simultaneously removes fines from the primary crusher and large particles from the secondary crusher discharge.

The crushed slag is sent to a storage bin, from which it is continuously fed to an open circuit rod mill. The 62.5 percent particulate emission from the rod mill is measured in a spiral classifier operating in a closed loop with a ball mill. The sands are re-ground in a ball mill and the slurry containing 80 percent minus 150 mesh is pumped into a conditioner where 0.2 lb KAX and 0.36 lb MIBC are added per ton of slag. The pulp is then floated in one stage to produce a coarser concentrate containing 21.7 percent copper and representing 96 percent copper recovery from the converter slag. The concentrate is concentrated, filtered and returned to the reverberant oven. The flotation tail is a waste of converter slag.

- ***Method of obtaining hardened slag***

The treatment of hardened slag is similar to that of slowly cooled slag, except for crushing. Slag from copper converters is removed into ladles, transported to an inclined machine and granulated by pouring it into a quenching chute. The size of the granular slag is small enough that a crushing step is not required. The grinding, grading and flotation steps are identical to those used in the processing of slowly cooled slag.

6. Conclusions

Based on the research carried out, the following conclusions can be drawn:

1. A technology has been developed for the extraction of copper metals from industrial slags. The technologies of preparation for beneficiation based on the method of separation of industrial slags have been improved.
2. The process of heat treatment of industrial slags in a reducing environment at a special temperature has been developed.
3. A technology has been developed for the extraction of metals based on the creation of a liquid slag at various temperatures.
4. It is noted that in the literature not enough attention is paid to the development of mathematical models of the technological process of extracting non-ferrous metals from waste slag.

References

[1] Grachev, V., & Turakhodjaev, N; Influence of liquid aluminum alloy treatment at temperatures up to 2000C in terms of the alloy structure and gas aluminum oxides content. International Journal of Mechanical Engineering and Technology, Volume 9, Issue 7, Pp: 489-495, 2018.

[2] Nodir, T., Sherzod, T., Ruslan, Z., Sarvar, T., & Azamat, B.; Studying the scientific and technological bases for the processing of dumping copper and aluminum slags. Journal of Critical Reviews, Volume 7, Issue 11, Pp: 441-444, 2020.

[3] Turakhodjaev, N., Tursunbaev, S., Tashbulatov, S., & Kuchkorova, M; Analysis of technological solutions for reducing the copper concentration in slags from oxygen-flare smelting of copper sulfide concentrates. Journal of Critical Reviews, Volume 7, Issue 5, Pp: 449-452, 2020.

[4] Sanakulov K. S., Khasanov A. S.; Processing of copper production slags-Tashkent: FAN, 2007. Metals The Metallurgy of the Common, Gold, Silver, Iron, Copper, Lead, and Zinc, by Leonard S. Austin. 2012.

[5] Karimov, K., Turakhodjaev, N., Akhmedov, A., & Tashbulatov, S.; A mathematical model of the technology of extraction of copper from industrial slags. In E3S Web of Conferences, Volume 264. EDP Sciences, 2021.

[6] Samadov A.U., Matkarimov S.T., Khudoyarov S.R., Berdiyarov B.T.; Studying methods of extraction iron and its compounds from steel-smelting slags, Proceedings of the international conference on integrated innovative development of Zarafshan region: achievements, challenges and prospects, Navoi, Pp: 182-184, 2017.

[7] Karimov, K., Akhmedov, A., Kushimov, B., & Yuldoshev, B.; Justification, development of new technology and design for drying seeds of desert fodder plants. In IOP Conference Series: Materials Science and Engineering (Vol. 883, No. 1, p. 012107). IOP Publishing, 2020, July.

[8] Тураходжаев, Н. Д., Ташбулатов, Ш. Б., Турсунбаев, С. А., Турсунов, Т. Х., & Абдуллаев, Ф. К.; Исследование анализа извлечения меди и алюминия из шлаков в дуговой печи постоянного тока. In Техника и технологии машиностроения, Pp: 68-70), 2020.

[9] Wang, Y., Zhang, S., Wu, R., Turakhodjaev, N., Hou, L., Zhang, J., & Betsofen, S.; Coarsening kinetics and strengthening mechanisms of core-shell nanoscale precipitates in Al-Li-Yb-Er-Sc-Zr alloy. Journal of Materials Science & Technology, Volume 61, Pp: 197-203, 2021.

[10] Wang, Y., Zhong, F., Wu, R., Wu, H., Turakhodjaev, N., Kudratkhon, B., ... & Zhang, M.; High-strength, ductility and modulus Al–Li/B4C composite with near nanostructure produced by accumulative roll bonding. Journal of Alloys and Compounds, 834, 155105, 2020.

[11] Wang, Y., Zhang, S., Wu, R., Turakhodjaev, N., Zhang, J., Liu, M., & Mardonakulov, S.; Concurrently improving uniform elongation and strength of ultrafine-grained Al–2Li alloy. Materials Science and Engineering: A, 792, 139848, 2020.

[12] Тураходжаев, Н. Д., Камолов, Ж. С., Тураходжаева, Ф. Н., Ташбулатов, Ш., & ЧОРШАНБИЕВ, Ш.; Тепловая схема плавки металла под слоем биологически активного флюса. O ‘Zbekiston Jurnali, 75, 1992.

[13] Ташбулатов, Ш. Б., Турсунбаев, С.А., & Чоршанбиев, Ш.М.; Влияние различных примесей и добавок на свойства меди, Техника и технологии машиностроения, 25-28, 2018.

[14] Тураходжаев, Н. Д., Ташбулатов, Ш. Б., Турсунбаев, С. А., Турсунов, Т. Х., & Абдуллаев, Ф. К.; Исследование анализа извлечения меди и алюминия из шлаков в дуговой печи постоянного тока. In Техника и технологии машиностроения, Pp: 68-70, 2020.

[15] Якубов, Л., Ташбулатов, Ш., Чоршанбиев, Ш. М., Тураходжаев, Н., & Тураходжаева, Ф. Н.; Разработка состава флюса для плавки медных сплавов. Композиционные материалы, Volume 4, P: 84, 2018.

[16] Wang, Y., Wu, R., Turakhodjaev, N., & Liu, M.; Microstructural evolution, precipitation behavior and mechanical properties of a novel Al–Zn–Mg–Cu–Li–Sc–Zr alloy. Journal of Materials Research,Volume 36, Issue 3, Pp: 740-750, 2021.

[17] Nodir, T., Sarvar, T., Andrey, J., & Yahyojon, M. (September); Mathematical Model for Calculating Heat Exchange. In International Conference on Reliable Systems Engineering, Pp: 243-249, Springer, Cham, 2021.

[18] Turakhodjaev, N., Tursunbaev, S., Turakhujaeva, A., Akramov, M., Turakhujaeva, S., & Kamalov, J.; Calculation of the heat exchange process for geometric parameters. International Journal of Mechatronics and Applied Mechanics, Volume 1, Issue 9, Pp: 90-95, 2021.

[19] Umidjon Mardonov, Muhammad Turonov, Andrey Jeltukhin, Yahyojon Meliboyev; The difference between the effect of electromagnetic and magnetic fields on the viscosity coefficients of cutting fluids used in cutting processes, International Journal of Mechatronics and Applied Mechanics, Issue 10, Volume 1, 2021.

[20] Umarov, E., Mardonov, U., Abdirakhmonov, K., Eshkulov, A., & Rakhmatov, B. (2021). Effect of magnetic field on the physical and chemical properties of flowing lubricating cooling liquids used in the manufacturing process. IIUM Engineering Journal, Volume 22, Issue 2, Pp: 327-338, 2021. doi: https://doi.org/10.31436/iiumej.v22i2.1768.

[21] Erkin, U., Umidjon, M., & Umida, S. (2021, September). Application of Magnetic Field on Lubricating Cooling Technological Condition in Metal Cutting Process. In *International Conference on Reliable Systems Engineering* (pp. 100-106). Springer, Cham.

[22] Karimov, Sh.A., Mamirov, Sh.Sh., Khabibullayeva, I.A., Bektemirov, B.Sh., Khusanov, N.; Friction and wear processes in tribotechnical system. International Journal of Mechatronics and Applied Mechanics, Issue 10, Vol. I, Pp: 204-208, 2021.