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COMPARATIVE TECHNOLOGICAL EVALUATION OF SCHEMES FOR THE ENRICHMENT OF OXIDIZED FERRUGINOUS QUARTZITES

Introduction

Oxidized ferruginous quartzites (OFQ) are not industrially processed in Russia, but are mined along with unoxidized and stockpiled with the formation of technogenic deposits, which creates a difficult environmental situation, so the issue of their involvement in processing is of particular relevance. The problem of using their huge reserves, including those in special dumps, is still unresolved. The obstacle for effective use of OFQ is not only organizational and economic issues, but also, first of all, the level of scientific preparation of the technology of their enrichment and practical readiness of the machine-building industry to provide the technology with modern enrichment equipment [1–6].

A set of studies on the comparative evaluation of the technological properties of oxidized quartzites of the Starooskolsky ore district of the KMA was carried out. The relative pulverizability of oxidized quartzites during the first stage of grinding to a fineness of 50% of the minus 0.045 mm class relative to non-oxidized ones of current production was established, which was 1.06–1.08 d. units. The comparative assessment of the enrichability was carried out according to three technological schemes: flotation → magneto-flotation → magnetic. The efficiency of enrichment of oxidized quartzites according to Hancock-Luiken, taking into account the fact that the initial ore contains several valuable components (martite, hematite, magnetite), is determined by the magnetic scheme as effective (n = 63.12%), by the magnetic flotation scheme as effective (n = 1.27%), by the flotation scheme as almost effective (n = 46.63%). According to the magnetic scheme of enrichment in a low- and high-intensity magnetic field, a concentrate with a maximum mass fraction of iron of 60.79% was obtained.

Keywords: oxidized ferruginous quartzites, martite, hematite, magnetite, technological properties (enrichability, pulverizability), low-intensity magnetic separation, high-intensity magnetic separation, flotation, concentrate, tailings

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As a rule, oxidized quartzites are characterized by significant differences in the material composition, variability of mineralogical varieties, a diversity of textural and structural features, nonuniform dissemination of ore and non-metallic phases, differences in physical and chemical and physical-mechanical properties. They are polymetallic raw materials in which the minerals of the ore phase (martite, hematite, goethite, magnetite, hydrohematite, hydrogoethite, limonite) are in close association and in various quantitative ratios with quartzites, magnetite, hydrohematite, hydrogoethite, limonite) are in close association and in various quantitative ratios with quartzites, magnetite, hydrohematite, hydrogoethite, limonite) are in close association and in various quantitative ratios with quartzites of the standard sample. To determine the relative grindability of oxidized quartzites, a sample of unoxidized quartzites from the current mining, representing the weighted average accumulated ore mixture by deposits and process samples, compiled from them bulk samples by deposit and a process sample. Bulk samples by deposit and a process sample are representative of the weighted average accumulated ore mixture for the year and consisting of magnetite (85%), iron-mica (4%) and silicate-magnetite (8%) quartzites, impoverishing rocks (3%) was accepted as the standard. The oxidized quartzites samples under study were evaluated by the coefficient of relative grindability $k_\text{rel}$, equal to the ratio of specific productivities by class minus 0.045 mm when grinding oxidized quartzites and quartzites of the standard sample. Sample preparation included compiling a standard sample, taking samples to determine the composition and properties of oxidized quartzites core samples, compiling from them bulk samples by deposit and a process sample. Bulk samples by deposit and a process sample for technological evaluation are made on the basis of extreme heterogeneity of oxidized quartzite, noted at the stage of their preparation for testing. The mass fraction of total iron in the initial samples ranged from 34.42 to 40.72%. A significant difference in the mass fraction of magnetic iron from 1.01 to 15.89% attracts attention, with a magnetic modulus $M$ varying from 0.03 to 0.40 unit fraction. According to the set of geological-mineralogical characteristics determining the technological properties, physical-chemical and physical-mechanical properties, the studied...
oxidized quartzites correspond to the composition and properties given in [2, 7, 8].

The technological sample of oxidized quartzites is compiled from the original core samples in proportion to the yield of their core. The technological sample was composed of favorable, in terms of enrichment, species. The sum of hard-to-enrich substantially sideritized quartzites and impoverishing rocks was about 10%. Representativeness of the technological sample depends on the key properties, which were determined by the coefficient of uniformity of mineralization distribution \( K_u \), which is taken as the ratio of the average mass fraction \( C_{av} \) of total iron to the maximum \( C_{max} \) in the intersection of the mineral body with a conventional borehole with a linear core output value of 254.4 m, expressed as a percentage: 
\[
K_u = 100 \frac{C_{av}}{C_{max}} = 100 \cdot \frac{37.36}{40.72} = 91.75\%.
\]

The mass fraction of minerals – carriers of the valuable component was: hematite and martite – 32.85%; magnetite – 10.7%; carriers of harmful impurities – apatite – 0.16% and iron sulfides – 0.12%; quartz – 41.5%.

The program of technological tests included: determining the grindability of oxidized quartzites relative to the grindability of unoxidized quartzites of current mining; studying the effect of grind size on enrichment performance in a low-intensity magnetic field (LIMF); studying the effect of magnetic field induction on enrichment performance in a high-intensity magnetic field (HIMF); studying the effect of grind size on final enrichment performance by magnetic means; identifying optimal flotation conditions; analyzing enrichment products and the test results.

Grindability was estimated by the value of the specific productivity of the newly formed class \(-0.045\) mm \( q_{35} \), kg/(l·h):
\[
q_{35} = 60P(\rho_{0.045} - \rho_{0.045})/(IV),
\]
where \( P \) is the weight of the load for grinding, kg; \( t \) is the grinding time, min; \( V \) is the mill volume, l; \( \rho_{0.045} \) is the mass fraction of the final class in the initial and milled sample, unit fraction.

The mass of the sample for grinding is determined by the formula:
\[
V = \frac{kD^2}{\delta\rho V},
\]
where \( k \) = 0.12 is the coefficient determining the share of the mill volume occupied by ore, unit fraction; \( \delta \) – ore bulk weight, kg/l.

The calculated mass of the sample for grinding is taken as 1.7 kg. Grinding was carried out at a solid-to-liquid ratio of 1 to 0.33. The weight of the ball load is determined by the formula
\[
G_b = \delta_b\rho V = 4.8 \cdot 0.4 - 7 = 13.4 = 13 \text{ kg},
\]
where \( \delta_b \) – bulk weight of balls, kg/l; \( \rho \) – ball fill factor of the mill, unit fraction.

To stabilize the particle size distribution of the mill feed, working particle size classes were allocated, from which the sample for the determination of the comparative grindability according to the average yield of each particle size class was composed.

Based on the average particle size distribution of the crushing products, we calculated the ball size:
\[
d_b = \frac{288d_{max}}{d_{max}},
\]
where \( d_b \), \( d_{max} \) are the balls diameter and size of the maximum lump coming for grinding, mm.

After each interval of grinding time, the granulometric characteristic of the material was determined, from which grindability curves were plotted.

In order to establish the dependence of technological parameters of enrichment on the coarseness of the initial ore a series of experiments of enrichment by magnetic method, crushed to different coarseness was carried out. Enrichment was performed by wet magnetic separation NIMS \( (H = 105 \text{ kA/m}) \) and HIMS \( (B = 1.15 \text{ T}) \) with the help of electromagnetic tubed analyzer 25T-SEM (“Mekhanobr”, Russia) and test bench HIMS with a working area in the form of a casette with fluted plates (NRU BelGU, Russia).

Flotation tests were performed by reverse cationic flotation in a cylindrical laboratory mechanical machine «WEMCO LAB CELL» (Dorr-Oliver Eimco, Avriniya) with a mechanical method of aeration and a set of interchangeable chambers. The main flotation was carried out in a chamber with a volume of 0.75 l, the reconditioning and the control flotation in 0.3 l chamber at a speed of the impeller 46 sec\(^{-1}\), with an air flow rate of 0.015 l/sec. Prior to flotation, the initial charge of a certain weight (taking into account the creation of the necessary density of the slurry) was soaked in recycled water for 12 hours.

A cationic collector RA-14 (Tomah, USA) was used as a cationic collector, which has proven itself in the conditions of PJSC “Mikhailovsky GOK” during additional enrichment of magnetite concentrate and tailings, as well as during pilot tests in the technology of flotation enrichment of oxidized quartzites. Modified corn starch (Zvyaginsky Starch Factory LLC, Russia) was used as iron oxide depressor, caustic soda was used as a medium regulator. The flotation reagents were prepared with distilled water and used as a freshly prepared 1.0% solution. Experiments on selection of optimal flotation mode were performed on recycled water, selected under conditions of current production at KMA enterprises, which was not softened (hardness up to 6.0 mg eq/dm\(^3\)).

**Grindability**

The average mass fraction of the final grade after crushing for oxidized quartzite was 15.87%; for unoxidized quartzite it was 17.98%. Calculation of the grindability was performed by the newly formed class \(-0.045\) mm relative to the standard sample (Table 1).

Industrial grinding coarseness of stage I is 50% of the class \(-0.045\) mm. The relative grindability of oxidized quartzites at a size of 50% of \(-0.045\) mm was 1.08 unit fraction, i.e., other things being equal, the productivity of head mills when grinding them will be higher than when grinding unoxidized quartzites by a maximum of 8%.

The target coarseness of the process sample of oxidized quartzite for flotation was 88% of the class \(-0.045\) mm. “Grindability curves” of the standard sample and oxidized quartzites of the process sample for flotation by the \(-0.045\) mm class are shown in Fig. 2. The specific capacity for the newly formed class \(-0.045\) mm when grinding to a given particle size of the technological sample for flotation was 0.246; the standard one was 0.232 kg/lh. Relative grindability of oxidized quartzites to the size of 88% of the class minus 0.045 mm was 1.06 unit fraction, i.e., under other equal conditions the productivity of head mills when grinding oxidized quartzites for flotation will be higher than when grinding unoxidized quartzites by maximum 6%.

**Enrichability**

The study of the effect of particle size reduction of oxidized quartzite on the enrichment performance of LIMS was carried out at grinding for 5, 15, 30, 45 and 60 minutes, the size range after grinding was 34.3–96.3% of the class \(-0.045\) mm. The
The main task of enrichment of oxidized quartzites in LIMS is the removal of magnetite from the process. The results of enrichment are given as a graphical dependence of technological indicators (yield, mass fraction of total and magnetic iron, extraction of total and magnetic iron in the concentrate) on the size of grinding (Fig. 3).

Proceeding from the main task of enrichment in LIMS, the main evaluation criterion of the effect of the size of crushing on the enrichment performance was determined by the extraction of magnetic iron in the concentrate, the maximum value of which fell within the size range of 55–60% of the class minus 0.045 mm and amounted to 97.96%.

The effect of magnetic field induction (B) in HIMS on the enrichment performance of LIMS tailings was studied. The mass fraction of total iron in them was 29.24; magnetic – 0.7%. The main task of stage I of HIMS enrichment is to produce tailings. The averaged results of enrichment of HIMS at different inductions are shown as a graphical dependence of enrichment indicators on the induction of the magnetic field (Fig. 4).

Stabilization of HIMS enrichment indicators occurs in the range $B = 0.65–0.95$ T. Creation and maintaining of VIMS implies significant expenditures of electric energy, therefore $V = 0.65$ T was accepted as optimal, at which the tails with mass fraction of total iron 12.6 and magnetic 0.09% were obtained, which allowed to consider them as dumping product.

Determination of the final particle size distribution required to obtain satisfactory enrichment performance was carried out by regrinding the HIMS stage I concentrate to a mass fraction of class $–0.045$ mm: 80, 85, 90, 95 and 100%.

The regrind concentrate was enriched in stage II of HIMS at $B = 0.65$ T in two steps (Fig. 5). The maximum mass fraction of total iron in the concentrate was obtained at a grinding coarseness of 95% of the $–0.045$ mm class and was 56%.

Thus, the scheme of enrichment of oxidized Figure 2. Grindability of process sample of oxidized quartzites relative to unoxidized of current mining

<table>
<thead>
<tr>
<th>Grinding parameters</th>
<th>Partial class yield minus 0.045 mm, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Southern deposit</td>
<td></td>
</tr>
<tr>
<td>Grinding time, min</td>
<td>11</td>
</tr>
<tr>
<td>Specific capacity by load, kg/h</td>
<td>1.325</td>
</tr>
<tr>
<td>Specific productivity by newly formed class, kg/h</td>
<td>0.437</td>
</tr>
<tr>
<td>Grindability coefficient by ore of current mining, unit fraction</td>
<td>1.180</td>
</tr>
<tr>
<td>Western deposit</td>
<td></td>
</tr>
<tr>
<td>Grinding time, min</td>
<td>12</td>
</tr>
<tr>
<td>Specific capacity by load, kg/h</td>
<td>1.214</td>
</tr>
<tr>
<td>Specific productivity by newly formed class, kg/h</td>
<td>0.401</td>
</tr>
<tr>
<td>Grindability coefficient by ore of current mining, unit fraction</td>
<td>1.080</td>
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<tr>
<td>Northwest deposit</td>
<td></td>
</tr>
<tr>
<td>Grinding time, min</td>
<td>15</td>
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<tr>
<td>Specific capacity by load, kg/h</td>
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<tr>
<td>Specific productivity by newly formed class, kg/h</td>
<td>0.321</td>
</tr>
<tr>
<td>Grindability coefficient by ore of current mining, unit fraction</td>
<td>0.870</td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>Grinding time, min</td>
<td>12</td>
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<td>Specific capacity by load, kg/h</td>
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<td>Specific productivity by newly formed class, kg/h</td>
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<td>Grindability coefficient by ore of current mining, unit fraction</td>
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<td>Ore of current production</td>
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<tr>
<td>Grinding time, min</td>
<td>13</td>
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<tr>
<td>Specific capacity by load, kg/h</td>
<td>1.121</td>
</tr>
<tr>
<td>Specific productivity by newly formed class, kg/h</td>
<td>0.370</td>
</tr>
</tbody>
</table>

Table 1. Average grindability results of oxidized quartzites compared to unoxidized current production

Fig. 3. Dependence of technological indicators on the particle size distribution
quartzites by magnetic method with the established optimal modes was as follows. The head of the scheme used LIMS pre-milled to 60% of the class minus 0.045 mm of oxidized quartzites for the extraction of magnetite to obtain a magnetite concentrate with a mass fraction of iron 66.4 at a yield of 21.7 and extraction of iron 38.63% (Fig. 6). The HIMS stage I operation with \( B = 0.65 \) T isolated waste tailings with a mass fraction of iron of 12.6 with yield of 41.89 and an iron loss of 14.22%.

Concentrate of stage I HIMS after regrinding to the size of 95% of the class minus 0.045 mm was subjected to operation of stage II HIMS in two steps at \( B = 0.65 \) T. As a result, a concentrate with a mass fraction of iron of 56.0 with a yield of 25.39 and iron extraction of 38.12% was obtained.

The obtained concentrate was combined with magnetite concentrate, the mass fraction of iron in which was 60.79; yield 47.09 and iron extraction 76.75%. Iron losses during enrichment according to the magnetic scheme amounted to 23.25; the yield of tailings was 52.91 with the mass fraction of iron 16.39%.

When simulating the magnetic flotation scheme, the magnetic middlings (hematite concentrate of stage I of HIMS) with a mass fraction of total iron 48.3 was regrind to a size of 95% of the class minus 0.045 mm. The regrind product was stirred for 3 minutes at a mass fraction of solid 30%, then contacted sequentially with the media regulator, iron oxide depressor, and collector for 3 minutes. The prepared flotation feed was fed to the main flotation in a closed cycle. The chamber product of the main flotation was recleaned in two steps, and the foam product was subjected to control flotation. The main and control flotation time was 6 min. Chamber product recleaning was carried out in the 1st step for 4 minutes, in the 2nd step - for 3.5 minutes until the foam depletion.

Flotation of the magnetic middlings resulted in a concentrate with a mass fraction of total iron of 51.4 with a total iron extraction of 43.42%. Iron losses amounted to 3.73% with the mass fraction of iron in the flotation tailings 28.73%.

Thus, according to the magnetic flotation scheme the combined concentrate with a mass fraction of total iron 57.46 with iron extraction of 82.05 and a yield of 53.26% was obtained. Loss of total iron with the tailings was 17.95; and the mass fraction of iron in them was 14.33%.

When simulating the flotation scheme of enrichment oxidized quartzites with a mass fraction of total iron 37.36%; crushed to a coarseness of 88% of the class –0.045 mm, were fed into a closed loop basic flotation in an alkaline environment. The chamber product of the main flotation was recleaned in three steps, and the foam product of the main flotation was subjected to control flotation. Time of the main and

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Fig. 4. Dependence of technological indicators of HIMS stage I enrichment on the magnetic field strength

Fig. 5. Dependence of technological indicators of HIMS stage II enrichment on the size of grinding

Fig. 6. Magnetic scheme of enrichment of a technological sample under laboratory conditions
control flotation – 6 min, recleaning of the chamber product was carried out in the 1st and 2nd stages for 4 min, in the 3rd stage – for 3 min. As a result, 56.41 of the initial feed of the flotation middlings with a mass fraction of total iron 51.4 and a total iron extraction of 77.61% were obtained. Tailings with a mass fraction of total iron of 19.19% and yielding 43.59% of the initial feed were isolated. Flotation middlings, regrinded to the size of 95% of the class minus 0.045 mm, after agitation for 3 minutes with the collector, were fed for flotation with recleaning of the chamber product in 2 steps and control flotation of the foam product. The time of the main and control flotation was 6 min, the recleaning of the chamber product in the first and second stages was carried out until the depletion of foam for 4 and 3.5 minutes, respectively. The result was a flotation concentrate with a mass fraction of total iron of 52.17; the extraction of total iron was 76.86%; the yield was 54.95%. Mass fraction of total iron in flotation tailings – 19.16%.

It should be noted that the foam product of recleaning operations in the regrinding cycle is characterized by the mass fraction of total iron 25.03% at a yield of 5.9%.

Removing this product to the tailings would probably increase the mass fraction in the flotation concentrate to 57.46% with a 70.95% iron recovery. Herewith, total iron losses with waste tailings increase by 5.91%; and the mass fraction of iron in them increases by 0.96%.

The enrichment efficiency of oxidized quartzite is determined by the well-known Hancock–Luyken formula based on the generally accepted classification (the enrichment process is very effective at $\eta > 75$; effective at $\eta > 50$; ineffective at $\eta < 25$) [9], according to the recommendation [7]:

$$\eta = \frac{100(\epsilon\beta)}{100 - \sigma_{\text{fin}}},$$

where $\sigma_{\text{fin}}$ is the amount of pure ore mineral in the initial ore, equal to: $\sigma_{\text{fin}} = \alpha\beta$, $\beta$ is the theoretical mass fraction of a useful element in a mineral, %.

When calculating the enrichment efficiency of oxidized quartzites, it was taken into account that the initial ore contains several recoverable minerals: martite, hematite, magnetite. Enrichment of oxidized quartzites by the magnetic scheme is defined as effective ($\eta = 63.12\%$) by the magnetic flotation scheme as effective ($\eta = 61.27\%$) by the flotation scheme as almost effective ($\eta = 46.63\%$).

### Conclusion

1. During the period of industrial development of deposits of the Starooskolsky ore district, oxidized quartzites were tested twice by the magnetic enrichment scheme. The test results are given in Table 2.

2. The material composition, textural and structural features, physical and physical-mechanical properties of oxidized quartzites have a wide range of indicators in the ore field of deposits.

3. The expected productivity of the head mills when grinding to a size of 50% class -0.045 mm, all other things being equal, is higher by about 8% compared to ore from current mining.

4. Oxidized quartzites were tested using magnetic → magnetic-flotation → flotation enrichment schemes (Table 3).

### References


FLOTATION EXTRACTION OF TIN FROM TAILINGS OF SULFIDE-TIN ORE DRESSING USING THERMOMORPHIC POLYMER*

Introduction

At the current state of tin ore enrichment in Russia, it is necessary to involve in processing mineral raw materials with a low content of valuable components, complex mineral composition and uneven inclusions of cassiterite. Now, the main source of tin in Russia is a man-caused raw material in the form of enrichment tailings of sulfide-tin ores with a tin content of 0.2–0.35%. Given the steady increase in tin prices on the world market, growth in inland consumption of metal and availability of raw materials, there is every reason to restore the domestic tin industry.

Specialists of the Uralmekhanobr Institute have developed a complex multi-stage scheme with the use of gravitational methods, table flotation, flotation and magnetic separation [1]. The high brittleness of cassiterite and its sludging ability leads to large tin losses with gravity tails. Cassiterite is extracted from gravity enrichment sludges by flotation, however, the tin losses with flotation tails are also high – about 15%. Thus, the extraction of cassiterite from sludge products and the search for an effective flotation method from tin-containing sludges is a topical scientific task, which includes the development of ways to enhance the contrast of minerals by modifying their surface with complexing reagents that provide selective flotation of non-ferrous, rare and precious metals into concentrates [2, 3].

To increase the flotation activity of cassiterite from fines, proposed is a method of preliminary selective concentration of sludge particles containing tin using a thermosensitive polymer with a phosphine group – TMPF. The peculiarity of the polymer is that when heated to 32–33 °C, the structure of its molecule changes, which leads to a transition from a liquid aggregate state to solid one; at the same time, the hydrophobic/hydrophobic parameters of the molecule change, resulting in the formation of solid hydrophobic particles [4, 5]. Researchers of IPKON have developed a technique for flotation separation of fines containing noble and non-ferrous metals in the presence of thermomorphic polymers with functional groups for gold and platinum [4–7]. Thermomorphic polymers were obtained based on N-isopropylacrylamide and N-acryloxy succinimide with the addition of a polymerization initiator [8–10].

Earlier studies on the cassiterite flocculation using a thermomorphic polymer have shown that TMPF is adsorbed

The possibility of using a thermomorphic polymer with a phosphine group as a collecting reagent for the selective concentration of tin during flotation enrichment of sulfide-tin tails was first investigated in the work. A detailed description of the experimental scheme of flotation concentration of sulfide-tin ore tailings and the reagent mode are given. The main mineral of tin is cassiterite, highly brittle and inclined to sludging, which leads to large losses of tin with tails; the granulometric composition of the initial tails of the Solnechnyi mining and processing plant has shown that 50% of the sample is represented by size grade of 0.04 mm. The output of a slimy product of 20 μm is 20% with a tin content of 0.46% (according to chemical analysis). This product is one of the sources of tin losses (up to 33.5%) in the flotation concentration process and requires additional technological solutions. It has been shown that the use of selective concentration of the +20 μm class using a thermomorphic polymer (TMPF) for flotation of tin ores allows not only to reduce the loss of tin with tin with tin classes, but also significantly increase the flotation rate of cassiterite and technological parameters when beneficiating mature tailings of sulfide-tin ore processing. The main tin flotation using TMPF results in obtaining a rough tin concentrate I with a content of 0.55% Sn and extracting 49% of the operation. Rough tin concentrate II with a content of 0.38% Sn and 42% recovery was obtained by reextraction using TMPF. The total recovery of tin in the combined rough tin concentrate amounted to 90.71% of the operation. Subsequent purification of the obtained concentrate and gravity enrichment on the table concentrator will make it possible to obtain the concentrates richer in tin content required for their further processing. Further research will be aimed at developing scientifically based technological solutions to improve the quality of rough tin concentrate and extracting tin from the sludge product – 0.02 microns using new reagent compositions.

Keywords: sulfide-tin tails, cassiterite, sulfide minerals, enrichment tails, flotation, reagents-collectors, thermomorphic polymer, selective concentration

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