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Sustainable Refractory Solutions—New Gunning Mixes Containing Circular Material

Closing the loop of raw material flows through a circular economy and thereby finding sustainable refractory solutions is one fundamental strategic pillar of RHI Magnesita. In the last years, a major effort has been undertaken to translate this approach into gunning mixes. The main challenge was to implement a significant amount of circular raw materials, while keeping the main properties of the gunning mixes on the same level, for example the refractory performance, adhesive properties, and machinery handling. By following these criteria in a systematic development process, it has been possible to create a new sustainable gunning mix portfolio with a reduced product carbon footprint of up to 85%. In an intense and comprehensive trial phase in the main steel producing units, namely electric arc furnaces, basic oxygen furnaces, and ladles, it was possible to fully prove this new refractory concept.

Introduction

With the targets of increasing sustainability and substantially reducing CO_2 emissions, RHI Magnesita entered into a joint venture with Horn & Co. Group, the industry leader when it comes to circular material processing. This partnership called MIRECO positions RHI Magnesita as a pioneer in circular economy solutions for the refractory industry. Both companies have been working together for many years, with RHI Magnesita having purchased the majority of its circular raw materials from Horn & Co. Group. As a result, a close and trustful relationship evolved over time, forming an ideal basis for a joint and sustainable future. This was a crucial step to pave the way towards RHI Magnesita's ambitious global target of achieving a 15% CO_2 emissions reduction by 2025, as amongst other measures the usage of circular materials significantly impacts this area. In this article factors that influence incorporating circular refractory materials in basic gunning mixes are discussed as well as the approaches taken to develop the new sustainable product portfolio.

Product Carbon Footprint

To provide increasing customer transparency, RHI Magnesita is calculating the product carbon footprint (PCF) of its refractory products and has implemented this information on the technical data sheets (see page 39). All emerging greenhouse gases are considered in these calculations, starting with the raw material extraction, followed by transportation, production, and packaging. Furthermore, the indirect emissions from the electricity used and externally purchased raw materials are included in the calculations—namely scope 1, 2, and 3 emissions. The so-called cradle-to-gate approach adopted excludes the final transportation from RHI Magnesita's production plants to the customer.

Once the refractory products have been shipped, this PCF can be considered as scope 3 emissions at the customer site. This means that the emissions value RHI Magnesita delivers can serve as a basis for further calculations in for example a steel plant, which will continue to gain importance in the near future. The PCF of our products will be reevaluated and recalculated on a regular basis.

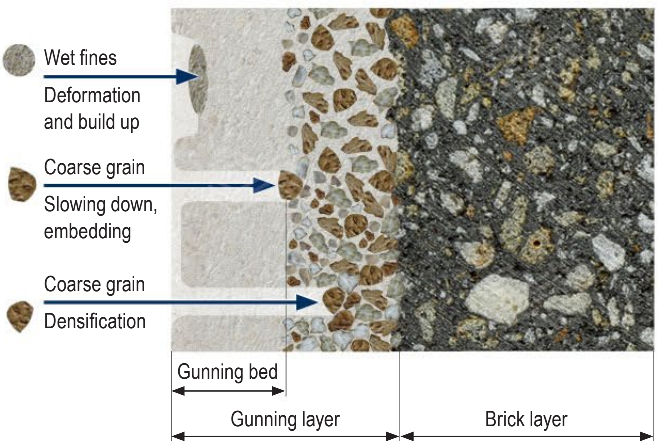
Basic Gunning Mixes and Their Fundamental Properties

In today's steelmaking plants, basic refractory gunning mixes are essential for the efficient operation of steel producing units [1]. The optimal choice of raw materials, a well-balanced grain size distribution, and an advanced binder system are crucial for the mix performance [2].

Grain size distribution

During the development of innovative gunning mixes it is essential to focus on an optimal distribution of all the fractions, which is necessary to achieve stable processing of the blend and to keep rebound at a very low level. The distribution of various grain sizes in a gunning bed is depicted in Figure 1.

Figure 1.
Formation of a gunning bed.



When adding circular raw materials to this equilibrium, all these aspects have to be considered. Hence, appropriate crushing and sieving of the used refractory material is very important to achieve the necessary balanced grain size distribution in the resulting circular raw material.

Bonding system

The binder system provides the required strength [3] until the ceramic bond formation takes place at temperatures above 1300 °C. In modern hot repair basic gunning mixes two binder systems are typical: The silicate bond and the phosphate bond.

Water soluble alkali silicates are the basis for the silicate binding system. They are moderate in terms of setting and therefore suitable for a broad range of application practices, ranging from a hand lance to semi-automated systems like the SHOOTER for basic oxygen furnace (BOF) maintenance or the TERMINATOR for electric arc furnace (EAF) repair.

Phosphates with varying acidity and degree of polymerisation are the basis for the phosphate-bonded gunning mixes. When using conventional phosphates such as sodium metasilicate, the applied gunning layer does not stabilise quickly and sufficiently [4]. However, this is necessary to ensure stiffening of the material and embedding of the coarse components. Therefore, it is crucial to choose a phosphate binder with the appropriate pH, because the more acidic the phosphate, the more strongly it reacts with the basic raw materials in the mix.

Raw material selection

One further aspect that influences the refractoriness of a basic gunning mix is the raw material selection. From 900 °C onwards, the chemical bonding phase weakens and sintering of the dead burned magnesia or the mixture of selected raw materials is mainly responsible for the strength and refractoriness. To develop high-quality gunning mixes, low-iron sintered magnesia with more than 90% MgO is often combined with alpine sintered magnesia that has a relatively high CaO/SiO_2 ratio. This high CaO/SiO_2 ratio prevents the formation of refractory-reducing, low-melting phases such as merwinite ($3CaO\ MgO\ 2SiO_2$) and monticellite ($CaO\ MgO\ SiO_2$).

Based on these basic gunning mix fundamentals, the question of how incorporating circular raw materials would influence the required properties arose.

MgO-C Circular Material in Basic Gunning Mixes

Up to now, the predominant opinion was that the wetting behaviour of circular MgO-C raw materials makes it impossible to use them in basic gunning mixes because of the negative effect on processing due to a low setting speed and initial adhesion. Therefore, a complete reexamination was required, including fundamental investigations on how circular materials could be implemented into basic gunning mixes.

The first approach to increase the gunning mix sustainability was to use leftovers that would otherwise have been landfilled. Therefore, detailed research on different material sources was performed to obtain a holistic overview of the chemical composition, including impurities. Additionally, microscopic investigations were carried out to gain information about the microstructural properties and the bonding structure, for example:

- Homogeneity of component distribution.
- Degree of ceramic bonding (e.g., fired products).
- Reactions between single minerals and components that had been exposed to high temperatures.
- Type and location of impurities.

From these investigations it could be concluded that the loss on drying (LOD) was relatively high, (i.e., up to 12%), and there was a huge variation in the main oxides such as MgO, CaO, SiO_2, and Al_2O_3, as well as the carbon content between different samples. However, the amount of heavy metals was negligible and no hexavalent chromium (Cr^{6+}) could be detected. After these investigations, the first test specimens were prepared to enable investigations on the final product characteristics. These specimens were based on the standard silicate-bonded ANKERJET GW gunning mix series and contained either very low or low addition of two circular raw material sources and different grain fractions. Reference specimens were prepared with the standard recipe for comparison.

Physical Characteristics of the First Test Specimens

During preparation of the first test specimens with MgO-C circular material, the high LOD caused serious crack formation as expected. To avoid this issue, a temperature treatment processing step of the circular material was implemented to significantly reduce the LOD before preparing the second series of test specimens. This led to a final LOD of less than 1%, which is the general upper limit for all materials and additives used in basic gunning mixes.

The outcome of the subsequent laboratory test series was a very important milestone in the project, as it showed the physical properties of the circular material containing specimens were comparable to the standard mix (Table I).

One further important aspect during selection and processing of circular raw materials is the grain size distribution. At this early stage of the project, special care was taken to ensure that the proportion of material below 0.3 mm was as low as possible, as this fraction of the carbon-containing material can cause a negative impact on the setting behaviour during application. From these investigations it could be concluded that any detrimental effect of MgO-C circular material in various quantities on the properties of the standard mix would be negligible in practical applications.

Thermochemical Calculations of Sustainable Mixes with a Process Slag

FactSage can be used to model the interaction between a refractory material and process media, for example the phase distribution in a gunning mix layer infiltrated by slag can be calculated. Since this thermodynamic modelling approach is based on a theoretical equilibrium, the results do not consider any kinetic modelling, mass transfer, or abrasion effects.

To investigate the interaction of different gunning mixes with a typical slag, the mix compositions shown in Table II were used, namely the standard ANKERJET GW mix was compared to two mixes based on the same grade, containing a low amount of MgO-C circular material, with or without carbon. The chemical composition of a customer's EAF process slag was analysed in house and used for the calculations. The results verified the conclusion given in the previous section, namely that the presence of carbon in the system does not have any negative impact on the thermodynamic balances.

First Gunning Trials at the Training Centre in Veitsch

Prior to any customer field trials, internal gunning trials at RHI Magnesita's training centre in Veitsch (Austria) were conducted to investigate the performance during application of the circular material containing gunning mixes. Special focus during these cold gunning tests was placed on the initial adhesion and the flowability of two circular material containing alternatives of the well-established ANKERJET RTW70-20-AT gunning mix. The prepared alternatives had a similar binding system, grain size distribution, and raw material content, and differed only in the circular material addition.

Table I.

Physical properties of different ANKERJET GW based specimens containing the MgO-C circular materials A or B, compared to the standard mix. Abbreviations include cold crushing strength (CCS), bulk density (BD), and porosity (POR).

Landfill source		A	B	A	B	A	B	A	B
Addition		Very low	Very low	Low	Low	Very low	Very low	Low	Low
Grain size (mm)		0.3–1	0.3–1	0.3–1	0.3–1	1–3	1–3	1–3	1–3
CCS [N/mm²]	20.9	22.0	35.8	16.0	23.1	12.1	24.5	17.4	21.0
BD [g/cm³]	2.29	2.35	2.61	2.28	2.51	2.31	2.57	2.33	2.53
POR [vol%]	33.74	32.16	24.88	34.25	27.71	33.33	25.87	32.80	26.75

Table II.

Chemical composition of the ANKERJET GW mixes used for the FactSage calculations.

	Standard ANKERJET GW [wt.%]	ANKERJET GW + low MgO-C addition [wt.%]	ANKERJET GW + low MgO-C addition (no carbon) [wt.%]
MgO	82.14	80.60	83.73
SiO_2	4.80	4.95	5.14
CaO	7.60	5.89	6.12
Fe_2O_3	3.70	2.55	2.65
Al_2O_3	1.20	1.71	1.78
Na_2O	0.56	0.56	0.56
C	0.00	3.74	0.00

Since availability of the landfill that could have served as a basis for the circular raw material was very limited at the time, standard MgO-C circular material from RHI Magnesita's Veitsch production plant was used. The advantages of this material were that the LOD was already below 1%, and could therefore be considered as "dry", it was available in optimised fractions, and it showed a constant chemical composition over time.

The results of these cold gunning tests showed no significant differences in the workability of all tested mixes. Especially the mix with the highest addition of MgO-C circular material showed excellent flowability and even required less water for an optimum consistency.

First Steel Plant Field Trials: Mixes Containing MgO-C Circular Material

To verify the positive outcome of the cold gunning trials and to test the performance at a customer, two circular material containing alternatives of the standard mix used by the customer were created. One of them contained a very low and one of them a low amount of circular material. The chemical compositions of the three mixes are shown in Table III.

The first trial was carried out at one of our European lead customers in an EAF with a tapping weight of approximately 100 tonnes, using a TERMINATOR with an average feeding rate of 120 kg/minute.

These tests showed a really promising performance, with the initial adhesion, rebound, and refractoriness on a comparable level to the standard mix. Especially between the two alternatives with different additions of circular material, no significant difference in the behaviour could be observed. However, to maintain the high-performance standards of RHI Magnesita's gunning mixes, at this point in the project the binding system was further optimised to avoid any spalling, particularly when the mix was applied to a low temperature surface. Figure 2 shows the spalling observed in the first test using the original binder system.

Conclusions from the first field trial with circular material containing mixes were:

- Slight spalling occurred prior to the binder system optimisation when applied to colder surfaces.
- Application of thicker gunning layers required an improved bonding system (i.e., faster setting).
- Service life depended on the production program but was equal to the standard ANKERJET RTW70-20-AT mix.
- Workability and refractoriness were excellent.

Follow-up trials took place under the same conditions, with the previously mentioned standard and circular material containing mix alternatives, but with the optimised binding system. As shown in Figure 3, no spalling occurred with the refined concept.

Table III.

Chemical composition of the ANKERJET RTW70-20 alternatives used to evaluate the performance of circular material containing mixes in a customer's EAF.

Alternative	Circular material addition	MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3	C
ANKERJET RTW70-20-AT		82.1	4.8	7.6	3.7	1.2	0.0
ANKERJET RTW70-20-VL	Very low	81.0	4.9	7.4	3.5	1.3	1.3
ANKERJET RTW70-20-L	Low	80.8	4.9	6.7	3.0	1.5	2.5

Figure 2.

Slight spalling observed during application on a low temperature surface in the first test using the original binder concept.

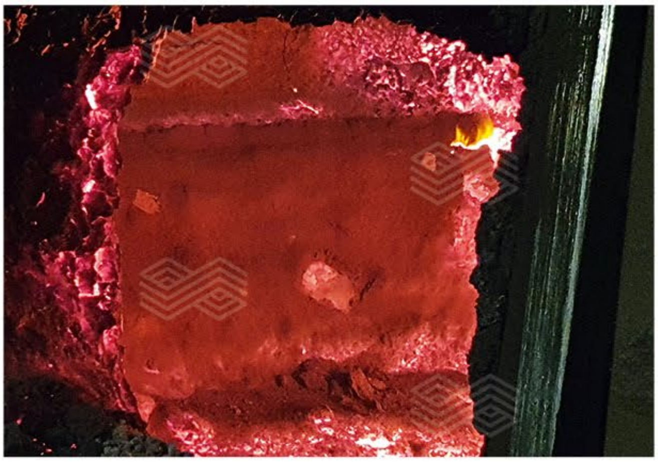


Figure 3.

Excellent sticking properties and no spalling observed in the second test using the optimised binder concept.

Following these very positive results, further customer trials were carried out including campaigns with up to 25 tonnes of trial material and significantly longer test phases. All tests showed at least the same refractoriness as the standard mix and it was concluded that the use of MgO-C circular material in basic gunning mixes had no negative impact on the workability.

Magnesia Spinel Circular Material in Basic Gunning Mixes

To achieve RHI Magnesita's goal of further reducing the carbon footprint of its products, another project was launched to find additional sources of circular raw materials suitable for basic gunning mixes. After considering all the important raw material factors, such as a stable chemical composition, a LOD below 1%, cost efficiency, and a secured supply chain in terms of availability and on-time shipment, it was decided to start an in-depth investigation of magnesia spinel circular material and its potential usage in refractory mixes.

Setting Test and Physical Values

The first step to investigate three different magnesia spinel types was the setting test, which determines the strength, setting behaviour, and temperature development when water is added to the gunning mix. In the initial approach, a 50/50 blend of the different magnesia spinel types with original raw materials was prepared, and the test was carried out on both a silicate- and a phosphate-bonded mixture. During these trials, there was no evidence that the magnesia spinel circular raw materials were detrimental, as all the relevant properties were within the known specifications.

Subsequently, different specimens were prepared that contained a medium and high proportion of magnesia spinel circular raw material in both silicate- and phosphate-bonded versions. To understand the processes induced by heat, the samples were exposed to different temperatures. These tests showed that the physical properties of the samples were not negatively affected when compared to the standard mixture, and although different levels of circular material addition showed different characteristics, no exclusion criteria were identified.

Steel Plant Field Trials: Mixes Containing Magnesia Spinel Circular Material

As the test results showed high potential, the next step was to carry out the first field trials in a steel plant. These trials were also performed in the EAF (tapping weight of approximately 100 tonnes) at one of our lead customers in Europe.

Five tonnes of each mix were tested, including silicate- and phosphate-bonded, medium, and high circular material containing gunning mixes. Following the experiences with the MgO-C circular material containing gunning mixes, the binding systems were optimised for the first field trials to ensure optimal material processing and adhesion.

All mixes showed excellent workability, such as primary adhesion—even on colder surfaces—and very low rebound (Figure 4). The refractoriness was validated during the test period and showed at least the same performance as the standard mix, with a tendency towards higher durability; however, this has to be verified in the future. Further trials with mixes containing high amounts of magnesia spinel circular materials were subsequently carried out in the 120-tonne EAF of another European customer and the positive results of the first tests were confirmed.

Sustainable Gunning Mix Portfolio

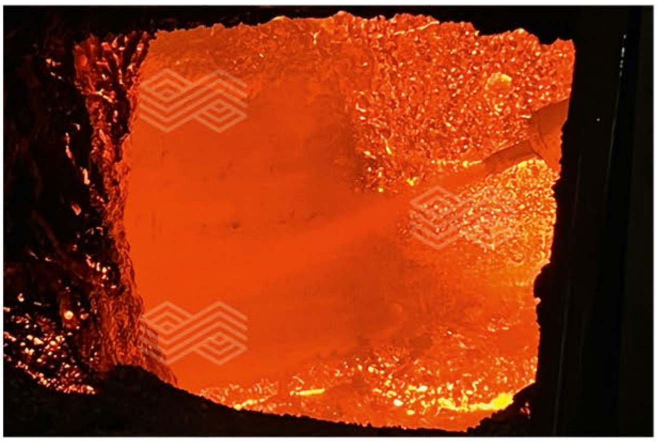
Due to the intense R&D activities, it was possible to implement completely new product types in the gunning mix portfolio, based on different amounts of MgO-C or magnesia spinel circular material. These solutions are paving the way towards a more sustainable future, by decreasing RHI Magnesita's scope 1 CO_2 equivalent (CO_2e) emissions, as well as customers' scope 3 emissions. Another aspect that increases the sustainability is being able to serve the European market with products produced in Europe—local for local—as the gunning mix product portfolio is currently available from the production plant in Veitsch.

MgO-C Circular Material Containing Gunning Mixes

To date, hundreds of tonnes of MgO-C circular material containing gunning mixes have been shipped and tested in customer applications across Europe and have proven that they can serve as a sustainable alternative to our standard gunning mixes without any performance decrease during application. Therefore, many customers are already using these products as their new standard gunning mix.

Figure 4.

Gunning mix with a high content of magnesia spinel circular material during application in an EAF.



In the current product portfolio, the higher amount of MgO-C circular material addition has been implemented, as the field trials showed equivalent performance to the standard mixes. With this well-established portfolio (Table IV), all European top selling gunning mix brands are covered.

Magnesia Spinel Circular Material Containing Gunning Mixes

After the positive laboratory tests and field trials, a product portfolio of magnesia spinel circular material containing gunning mixes has been implemented (Table V). With this portfolio, RHI Magnesita can provide customers with basic gunning mixes that have a drastically reduced PCF of up to -85% compared to the equivalent standard mix. Currently, the portfolio covers the high-performance silicate- and phosphate-bonded standard gunning mixes; however, due to the high sustainability potential and positive field trials, the portfolio will be extended.

Potential CO_2e Savings by Using Sustainable Gunning Mixes

The decreased PCF of RHI Magnesita's sustainable gunning mixes has a direct impact on the scope 3 emissions of the customers' steel plant. This means that by switching from a standard basic gunning mix to one of the above-mentioned developments, a customer's scope 3 emissions can be significantly reduced.

Table IV.
Sustainable gunning mix portfolio based on MgO-C circular material.

Grade	Application	Circular raw material content	Average PCF reduction	Description
ANKERJET YP12-AT	Standard gunning	Low	- 11%	Phosphate-bonded, high-performance gunning mix
ANKERJET YW12-AT	Standard gunning	Low		Silicate-bonded, high-performance gunning mix
ANKERJET YRW72-AT	Standard gunning	Low		Silicate-bonded, standard-performance gunning mix
ANKERJET YRW12-AT	Standard gunning	Low		Silicate-bonded, medium-performance gunning mix
ANKERJET YRP12-AT	Standard gunning	Low		Phosphate-bonded, medium-performance gunning mix
ANKERJET YKW72-AT	BOF mouth and ladle lip ring gunning	Low		Silicate-bonded ladle lip ring/ BOF mouth gunning mix

Table V.
Sustainable gunning mix portfolio based on magnesia spinel circular material.

Grade	Application	Circular raw material content	PCF reduction	Description
ANKERJET XW15-AT	Standard gunning	Medium	-40%	Silicate-bonded, high-performance gunning mix
ANKERJET XW10-AT	Standard gunning	High	-85%	
ANKERJET XP15-AT	Standard gunning	Medium	-40%	Phosphate-bonded, high-performance gunning mix
ANKERJET XP10-AT	Standard gunning	High	-85%	

Figure 5 gives an indication of the CO_2e savings a steel plant in Europe has achieved by changing from ANKERJET GW15-AT to one of the MgO-C circular material containing grades as the new standard. These calculations are based on the annual EAF gunning mix consumption of approximately 330 tonnes per year (EAF tapping weight approximately 150 tonnes). As illustrated in the diagram, the customer is saving 53 tonnes of CO_2e per year, which is an emission equivalent of a standard diesel car going around the world more than six times (assuming an average consumption of 8 litres per 100 km and emissions of 2.68 $kgCO_2e$/litre).

If the same steel plant switched to using one of the magnesia spinel containing gunning mixes, the CO_2e savings would increase to nearly 400 tonnes (Figure 6), which is an emission equivalent of a standard diesel car going around the world more than 45 times.

Conclusion and Outlook

Based on detailed R&D, RHI Magnesita has implemented completely new product lines for basic gunning mixes that are paving the way towards a more sustainable future. Through this new but well-established portfolio, customers are able to choose refractory products with lower PCFs and thereby minimise their scope 3 emissions. Due to the continuously increasing demand, RHI Magnesita is working on expanding these product lines to the production plant in Eskisehir (Turkey), thereby enabling further markets to be supplied with regional and sustainable products. To exploit the full potential of circular materials, additional investigations will be performed to determine the capabilities and limits of use, which will lead to an ever-growing sustainable product portfolio for basic gunning mixes as well as other refractory products.

Figure 5.

Annual CO_2e savings achieved by using ANKERJET YW12-AT, which contains a low amount of MgO-C circular material.

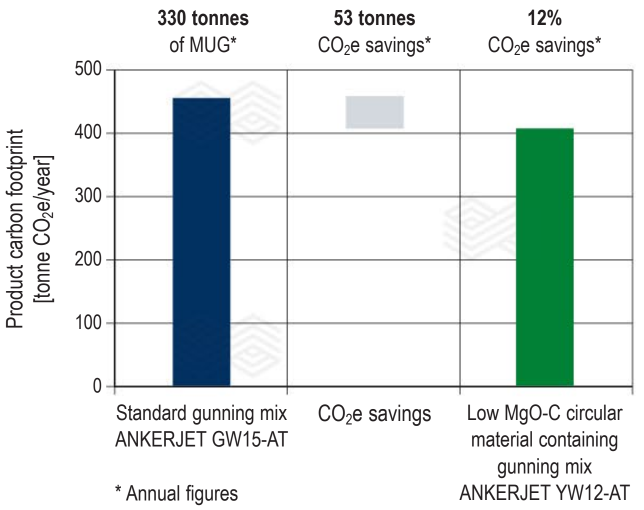
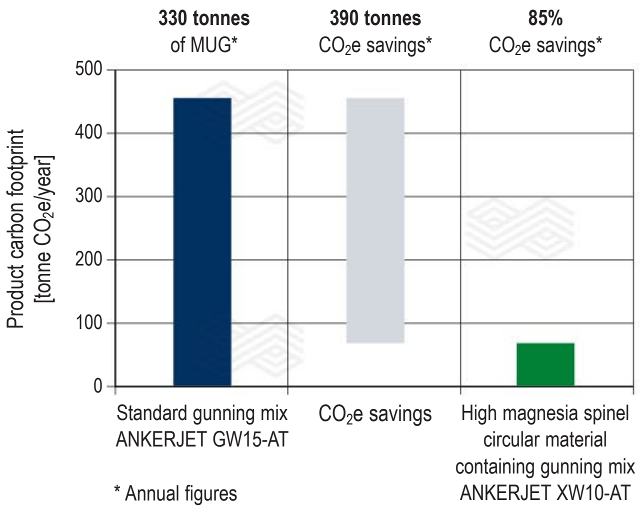


Figure 6.

Theoretical annual CO_2e savings that could be achieved by using ANKERJET XW10-AT, which contains a high amount of magnesia spinel circular material.



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