

## PHOSPHORUS IN MAGNETITIC IRON ORES: OCCURRENCE, PROCESSING CHALLENGES, AND SEPARATION STRATEGIES.

**Antonio Clareti Pereira**

PhD in Chemical Engineering

São Paulo University - USP

Belo Horizonte – MG – Brazil

E-mail: [claretipereira@gmail.com](mailto:claretipereira@gmail.com)

<https://orcid.org/0000-0001-8115-4279>

### Abstract

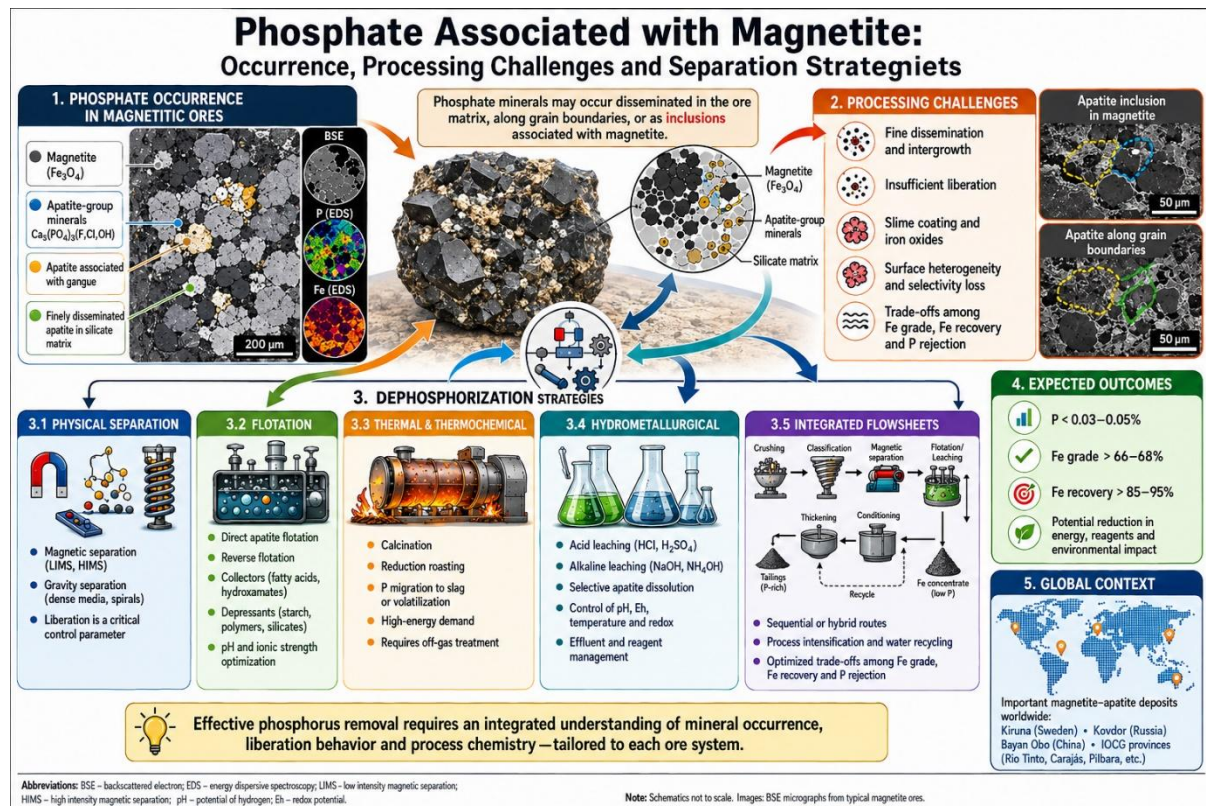
Phosphorus remains one of the most problematic impurities in iron ore processing because it degrades steel ductility, cold-workability, weldability, and fracture resistance. High-phosphorus magnetitic iron ores occur in several regions worldwide, including China, Australia, Brazil, Iran, Russia, and parts of Africa, where apatite, fluorapatite, and other phosphate minerals may occur as disseminated gangue phases, fine intergrowths, composite particles, or inclusions associated with iron-bearing minerals. Despite decades of investigation, phosphorus removal remains challenging because dephosphorization efficiency depends not only on the beneficiation route selected but also on mineralogical texture, liberation behavior, particle-size distribution, and surface chemistry. This review critically evaluates the modes of occurrence of phosphorus in magnetite iron ores and compares physical, flotation, thermal, thermochemical, hydrometallurgical, and integrated dephosphorization strategies. Particular attention is given to the relationship between mineralogical characteristics and beneficiation performance, including phosphorus removal efficiency, iron recovery, energy demand, reagent consumption, and technological maturity. The review also discusses industrial limitations, scale-up constraints, environmental implications, and the lack of integrated geometallurgical approaches in the literature. The analysis demonstrates that flotation remains the dominant beneficiation route, although its effectiveness decreases substantially in ores containing finely disseminated apatite and complex intergrowth textures. Integrated beneficiation circuits that combine mineralogical characterization, selective liberation, and hybrid processing routes appear more promising for industrial implementation.

**Keywords:** Magnetitic iron ore; Phosphorus; Apatite; Dephosphorization; Iron ore beneficiation; Flotation

### Highlights

- Mineral liberation controls phosphorus removal more strongly than process route selection.
- Flotation efficiency decreases substantially in ores containing fine apatite intergrowths.
- Thermal and hydrometallurgical routes remain constrained by energy and effluent costs.
- Integrated geometallurgical approaches remain insufficiently explored at an industrial scale.

## Graphical abstract



## 1. Introduction

Iron ore remains the primary raw material for steel production, and magnetite ores continue to account for a major share of global iron resources because of their high iron grades, magnetic susceptibility, and suitability for concentration processes. Large magnetite deposits occur in banded iron formations, iron oxide-apatite systems, skarn deposits, and metamorphic iron ore provinces across China, Brazil, Sweden, Russia, Chile, Australia, and Iran. Many of these deposits contain phosphorus-bearing minerals, particularly apatite and fluorapatite, which degrade downstream metallurgical performance and steel quality.

Phosphorus is generally considered a deleterious impurity in steelmaking because excessive concentrations reduce ductility and toughness while increasing cold brittleness and susceptibility to cracking. Typical industrial phosphorus specifications for premium steels are often below 0.02–0.05 wt.% P, depending on the final steel application and refining route. Consequently, iron concentrates with elevated phosphorus levels often require additional beneficiation, blending, or metallurgical treatment before entering blast-furnace or direct-reduction operations. Ofoegbu (2019a) demonstrated that high-phosphorus iron ores pose both

metallurgical challenges and economic constraints, as phosphorus removal often increases processing complexity and operating costs. Pereira and Papini (2015) also emphasized that phosphorus behavior varies substantially with mineralogical occurrence and the beneficiation route.

The occurrence of phosphorus in magnetite-iron ores is considerably more complex than often described in simplified beneficiation studies. In some ores, phosphorus occurs as liberated apatite grains associated with silicate gangue. In other cases, phosphate minerals appear as fine disseminations, microinclusions, composite particles, or intergrowths with magnetite and hematite. Several studies of magnetite-apatite systems from Kiruna-type deposits, IOCG environments, and iron oxide-apatite systems have shown that textural relationships strongly influence beneficiation behavior (Broughm et al., 2017; Tornos et al., 2017; Huang & Beaudoin, 2019). Fine dissemination often prevents complete liberation even under intense grinding, reducing beneficiation selectivity and increasing iron losses.

Another important issue is the discrepancy between laboratory-scale beneficiation studies and industrial performance. Numerous investigations report phosphorus removal efficiencies of 70–90% under highly controlled experimental conditions, using finely ground materials, optimized reagent dosages, or combined beneficiation routes. However, industrial operations often achieve lower selectivity because of ore variability, slime generation, incomplete liberation, fluctuating mineralogy, and operational constraints related to energy consumption and water recirculation. Donskoi et al. (2022) observed that high-phosphorus Australian iron ore fines exhibit beneficiation limitations related to particle texture and fine mineral dissemination. Similar constraints were reported in studies of Chinese oolitic ores and refractory phosphorus-bearing iron systems (Tang et al., 2016; Pan et al., 2022; Wu et al., 2026).

The beneficiation of phosphorus-bearing magnetite ores has traditionally focused on magnetic separation and flotation. Magnetic separation exploits the strong magnetic susceptibility of magnetite relative to gangue minerals. Nevertheless, apatite disseminated within magnetite-rich particles substantially reduces separation efficiency. Flotation has therefore become one of the most widely studied approaches for selective phosphorus removal because apatite surface chemistry can be modified using collectors, depressants, and pH regulators. Ruan et al. (2019) and Derqaoui et al. (2022) reviewed flotation reagents for

phosphate systems and highlighted the sensitivity of apatite flotation to water chemistry, slime coating, reagent adsorption, and surface oxidation.

Thermal, thermochemical, and hydrometallurgical routes have also been proposed to address the beneficiation limitations of complex phosphorus-bearing ores. Reduction roasting followed by magnetic separation, selective leaching, microwave-assisted liberation, and alkaline treatment have shown promising laboratory results under certain conditions (Cai et al., 2018; Tang et al., 2016; Hu et al., 2025d). Nevertheless, many of these routes remain constrained by high energy intensity, reagent consumption, effluent generation, and limited industrial validation.

An additional limitation in the current literature is the insufficient integration of mineralogical characterization and beneficiation design. Several studies compare dephosphorization routes without adequately considering the degree of liberation, particle texture, mineral associations, and ore variability. Automated mineralogical tools such as MLA and QEMSCAN increasingly show that process performance cannot be interpreted solely from bulk chemical analyses. Krolop et al. (2019) showed that automated mineralogical characterization provides critical insights into apatite distribution, particle locking, and liberation behavior in iron oxide-apatite systems.

This review critically evaluates the occurrence of phosphorus in magnetite iron ores and examines how mineralogical associations control beneficiation performance. It compares physical separation, flotation, thermal, thermochemical, hydrometallurgical, and integrated processing routes, emphasizing industrial applicability, process limitations, and scale-up constraints. Particular attention is given to the relationships among mineralogy, liberation behavior, process selectivity, and operational performance. The next section presents the methodology used for literature selection and comparative analysis.

## **2. Methodology**

This review was developed using a PRISMA 2020-informed methodology adapted for critical review studies in mineral processing, extractive metallurgy, and process mineralogy. The methodological approach was designed not only to identify relevant publications on phosphorus occurrence and dephosphorization of magnetite-bearing iron ores but also to critically evaluate the relationships among mineralogical characteristics, liberation behavior, beneficiation performance, industrial applicability, and process limitations.

Literature searches were conducted using the Scopus, Web of Science, ScienceDirect, SpringerLink, and Google Scholar databases, covering the period from 2000 to 2026. Classical studies published before 2000 were selectively included when deemed fundamental to understanding apatite mineralogy, phosphorus occurrence, magnetite beneficiation, flotation chemistry, or the fundamentals of thermochemical processing. Only peer-reviewed journal articles, conference papers with sufficient technical detail, and selected industrial reports were considered for the main comparative assessment.

The search strategy combined multiple keywords and Boolean operators to improve coverage of mineralogical, beneficiation, and metallurgical aspects of phosphorus-bearing magnetite ores. The principal search terms included “phosphorus in magnetite ores,” “phosphorus removal from iron ore,” “apatite flotation,” “magnetite–apatite deposits,” “dephosphorization,” “reduction roasting,” “magnetic separation,” “hydrometallurgical dephosphorization,” “process mineralogy,” “QEMSCAN,” and “liberation analysis.” Additional combinations, including “iron ore beneficiation,” “apatite intergrowth,” “slime coating,” “roasting–leaching,” and “integrated beneficiation,” were also used to identify studies addressing process integration and operational limitations.

The literature screening process prioritized studies reporting quantitative beneficiation and mineralogical data. Publications were considered eligible for detailed comparative analysis if at least one of the following parameters was reported: phosphorus removal efficiency, iron recovery, iron concentrate grade, reagent consumption, particle size distribution, liberation degree, energy demand, water consumption, or mineralogical characterization results. Particular emphasis was placed on studies that integrate process mineralogy with beneficiation performance, using MLA, QEMSCAN, SEM-EDS, XRD, Raman imaging, automated liberation analysis, or related characterization techniques capable of directly evaluating apatite occurrence and mineral locking behavior.

Studies focused exclusively on descriptive geology or ore genesis without implications for beneficiation were excluded from the main comparative analysis. However, selected references were retained to support discussions of mineralogical occurrence and deposit characteristics. Additional exclusion criteria included insufficient methodological description, lack of analytical validation, unsupported beneficiation claims, lack of reproducibility, or incomplete reporting of process conditions. Particular attention was given to distinguishing laboratory-scale investigations from pilot-scale or industrial applications, as many reported

promising laboratory efficiencies without demonstrating industrial scalability or operational stability.

Figure 1 summarizes the PRISMA 2020-based literature screening workflow used to identify studies relevant to phosphorus occurrence and beneficiation in magnetite iron ores.

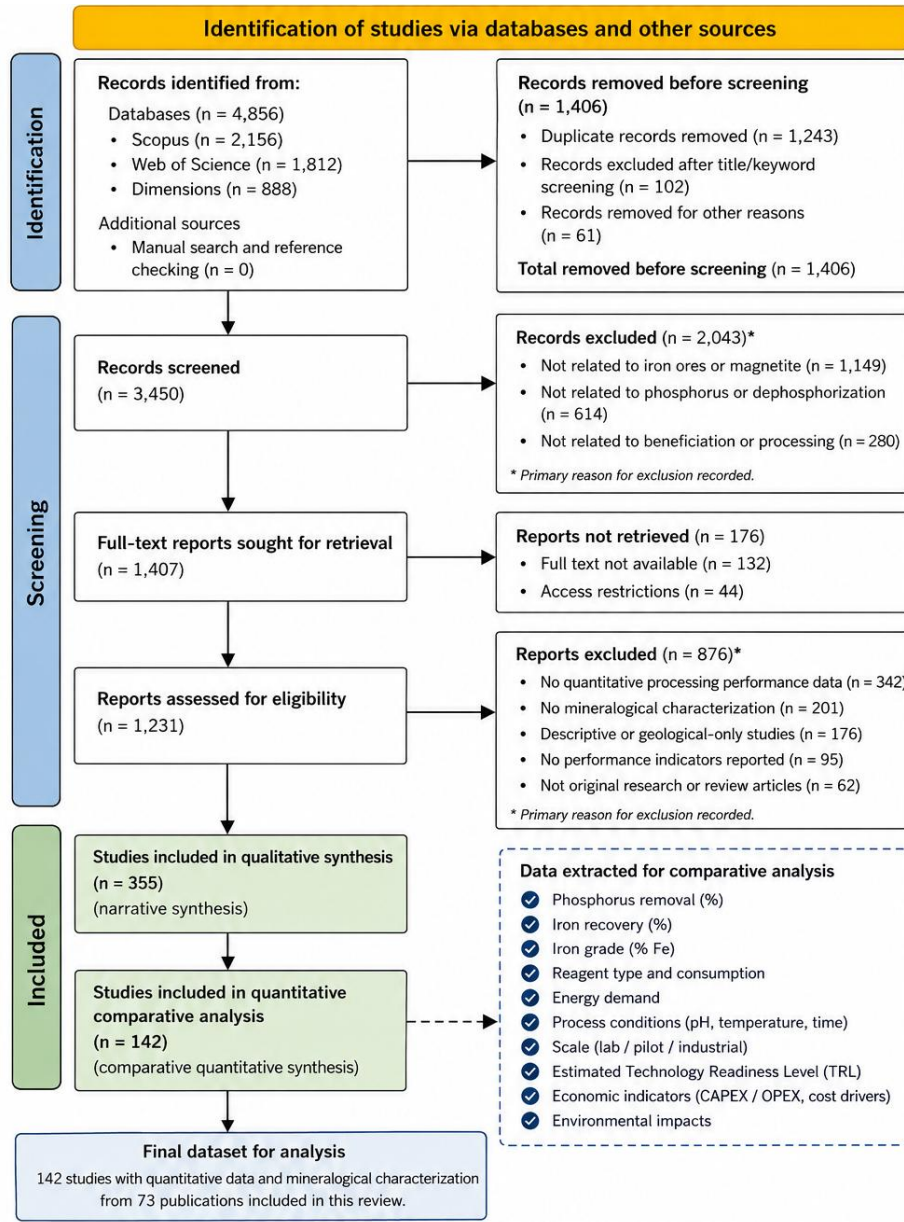


Figure 1. PRISMA 2020-based literature selection workflow for phosphorus removal studies in magnetitic iron ores. Adapted from Page et al. (2021).

The screening process revealed a strong concentration of publications on flotation chemistry, magnetic separation, and reduction roasting of high-phosphorus iron ores, particularly Chinese oolitic systems. In contrast, relatively little attention has been devoted to integrated geometallurgical characterization, predictive liberation modeling, industrial-scale

process integration, and long-term operational performance. Another important observation is the imbalance between laboratory experimentation and industrial validation. Many investigations reported high phosphorus-removal efficiencies under tightly controlled experimental conditions, using fine grinding, optimized reagent dosages, or aggressive thermochemical treatments, while offering limited discussion of energy consumption, reagent recycling, water management, scale-up constraints, or environmental implications.

To preserve the manuscript's critical-review character, the selected studies were evaluated comparatively across beneficiation route, mineralogical occurrence, liberation behavior, process maturity, operational limitations, environmental implications, and industrial applicability, rather than solely on phosphorus-removal efficiency. This comparative approach identified recurring limitations, including fine apatite dissemination, slime generation, composite particle formation, incomplete liberation, process integration complexity, and discrepancies between laboratory and industrial performance. The following section discusses the principal occurrence modes of phosphorus in magnetite-bearing iron ores and their implications for beneficiation behavior.

### **3. Occurrence, Process Mineralogy, and Liberation Behavior of Phosphorus**

Phosphorus in magnetite-bearing iron ores occurs in several mineralogical modes, ranging from liberated apatite grains to complex intergrowths with iron-bearing minerals. Understanding these modes is essential because beneficiation performance is controlled primarily by liberation behavior, mineral associations, and surface heterogeneity rather than by bulk phosphorus concentration alone. Several beneficiation failures reported in industrial operations are directly attributable to insufficient characterization of phosphorus distribution, apatite occurrence, and particle-locking behavior (Ji et al. 2024a).

In many magnetite-bearing iron ores, apatite is the dominant phosphorus-bearing mineral. Apatite may occur as disseminated grains associated with silicate gangue, as fine inclusions within magnetite-rich particles, as veinlets, fracture fillings, or as composite particles formed during metamorphic and hydrothermal processes. Studies of Kiruna-type and iron oxide–apatite deposits have shown that apatite occurrence varies substantially with ore genesis, alteration history, and structural deformation (Brough et al., 2017; La Cruz et al., 2019; La Cruz, 2019; Pietruszka et al., 2023). In some systems, apatite forms coarse, liberated grains

that are favorable for beneficiation. In others, apatite occurs as ultrafine microdisseminations that require extremely fine grinding for liberation.

Several investigations also showed that phosphorus-bearing phases may occur outside direct association with magnetite. In many ores, phosphate minerals are distributed within silicate gangue matrices or concentrated along grain boundaries rather than enclosed within magnetite crystals. Consequently, the assumption that phosphorus is always structurally associated with magnetite oversimplifies the beneficiation problem. Ofoegbu (2019b) emphasized that high-phosphorus ores exhibit substantial mineralogical variability, which directly affects beneficiation response and process selectivity.

Textural relationships strongly influence beneficiation performance. Fine-grained intergrowths often produce composite particles even after intense grinding, reducing magnetic separation efficiency and complicating flotation. Krolop et al. (2022) observed that liberation characteristics in Per Geijer iron oxide–apatite deposits varied substantially with particle size fraction and ore texture. Similar conclusions were reported for Kovdor apatite–magnetite systems and several Chinese refractory phosphorus-bearing ores (Ivanyuk et al., 2016; Mitrofanova et al., 2023).

Mineralogical characterization is therefore a critical step before selecting a beneficiation route. Automated mineralogical tools such as MLA and QEMSCAN enable quantitative evaluation of liberation degree, mineral associations, particle composition, and grain-size distribution. Raman imaging, SEM-EDS mapping, XRD analysis, and automated liberation analysis further aid in identifying phosphorus-bearing phases and their textural relationships with magnetite and gangue minerals.

Table 1 summarizes the primary occurrence modes of phosphorus in magnetite-bearing iron ores and their implications for beneficiation performance.

Table 1. Principal occurrence modes of phosphorus in magnetite-bearing iron ores and their implications for beneficiation performance. Adapted from Broughm et al. (2017), Krolop et al. (2019), Ofoegbu (2019a), and Krolop et al. (2022).

Occurrence mode	Typical mineral	Liberation behavior	Beneficiation implication
Disseminated apatite	Fluorapatite	Moderate	Favorable for flotation
Fine intergrowth	Apatite-magnetite	Difficult	Requires fine grinding
Inclusions	Apatite in magnetite	Very difficult	Poor selectivity
Gangue-associated phosphate	Apatite/silicates	Variable	Dependent on texture
Fracture filling	Secondary phosphate	Relatively favorable	Selective removal possible

The data summarized in Table 1 show that liberation behavior varies substantially by occurrence mode. Ores with coarse-liberated apatite generally exhibit higher flotation selectivity and lower grinding requirements. In contrast, ores with fine inclusions or composite particles often require ultrafine grinding, which increases slime generation and degrades flotation performance.

Figure 2 illustrates representative textural associations between apatite and magnetite and their influence on liberation behavior during beneficiation.

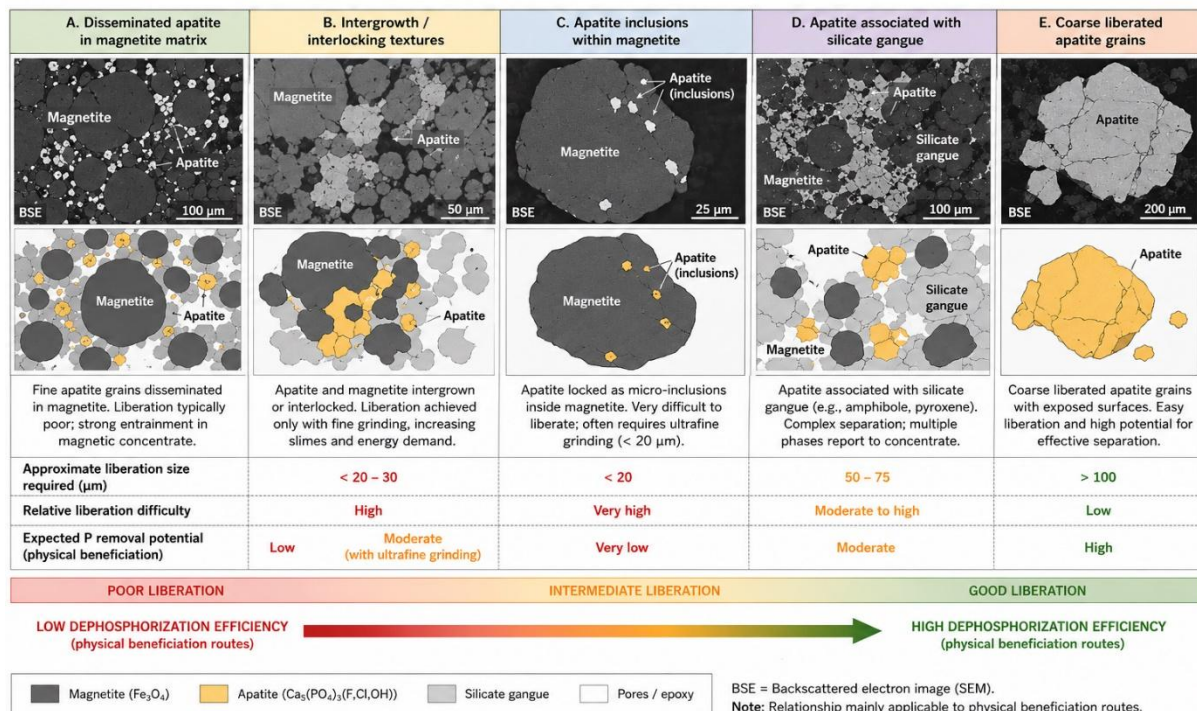


Figure 2. Typical textural associations between apatite and magnetite affect liberation and phosphorus removal efficiency. Adapted from Krolop et al. (2019), La Cruz et al. (2020), and Shi et al. (2024).

The textures shown in Figure 2 demonstrate that beneficiation performance cannot be generalized solely from phosphorus concentration. Ores with similar phosphorus grades may show markedly different beneficiation responses because liberation behavior depends on grain size, inclusion frequency, and particle locking. Consequently, mineralogical characterization must precede the selection of the process route. This mineralogical dependency directly affects the performance of the physical beneficiation routes discussed in the next section.

### 3.1. Relationship Between Mineral Liberation and Phosphorus Removal Efficiency

The relationship between mineral liberation and phosphorus-removal efficiency is one of the most critical factors governing beneficiation performance in magnetite-bearing iron ores.

Although phosphorus concentration is commonly used as an ore-quality indicator, beneficiation efficiency is fundamentally governed by the textural distribution of phosphorus-bearing minerals, the degree of liberation, and the formation of composite particles during comminution. Consequently, ores with similar phosphorus grades may exhibit substantially different beneficiation responses depending on the apatite occurrence mode, grain-boundary characteristics, and particle locking behavior (Ji et al., 2024b; Kalashnikov et al., 2016).

The degree of liberation directly affects the selectivity of both physical and physicochemical beneficiation routes. In magnetic separation systems, incomplete liberation promotes the recovery of apatite-bearing composite particles into the magnetic concentrate, thereby increasing phosphorus contamination even under high magnetic recovery conditions. Similarly, flotation performance strongly depends on the extent of apatite surface exposure available for collector adsorption. Fine intergrowths and locked particles reduce flotation selectivity because gangue and magnetite surfaces remain partially exposed, increasing entrainment and reagent consumption (Li et al., 2020).

Several investigations have shown that liberation thresholds vary substantially with ore texture and mineralogical associations. Coarse-grained apatite associated with silicate gangue may be liberated at relatively coarse grinding sizes (>75–100  $\mu\text{m}$ ), whereas apatite inclusions enclosed within magnetite frequently require ultrafine grinding below 20–30  $\mu\text{m}$ . However, excessive grinding introduces additional operational limitations, including slime generation, surface oxidation, particle aggregation, and increased water and reagent consumption. Consequently, beneficiation performance often exhibits an optimal liberation window rather than continuous improvement as particle size decreases (Karimzadeh et al., 2023).

The influence of liberation behavior also varies by beneficiation route. Physical separation methods such as LIMS, WHIMS, and gravity concentration are highly sensitive to incomplete liberation because composite particles may respond similarly to liberated magnetite. Flotation systems are also affected by surface heterogeneity, slime coating, and dissolved ionic species, particularly in ultrafine particle fractions. In contrast, hydrometallurgical routes may partially overcome liberation constraints through selective dissolution mechanisms, although process selectivity, reagent consumption, and iron losses remain important operational challenges (Li et al., 2025a).

Process mineralogy studies using MLA, QEMSCAN, SEM-EDS mapping, and automated liberation analysis consistently show that liberation behavior is a stronger predictor

of beneficiation performance than bulk phosphorus concentration alone. Krolop et al. (2022) and Mitrofanova et al. (2023) reported that ores with high proportions of binary and ternary apatite–magnetite associations exhibited significantly lower phosphorus-removal efficiencies despite similar overall phosphorus grades. Similar observations were reported for Kiruna-type and Kovdor apatite–magnetite systems, where liberation-controlled beneficiation behavior strongly influenced concentrate quality and process-route selection (Mondal, 2019).

Figure 3 presents a conceptual relationship between the degree of liberation and phosphorus removal efficiency across different beneficiation routes.

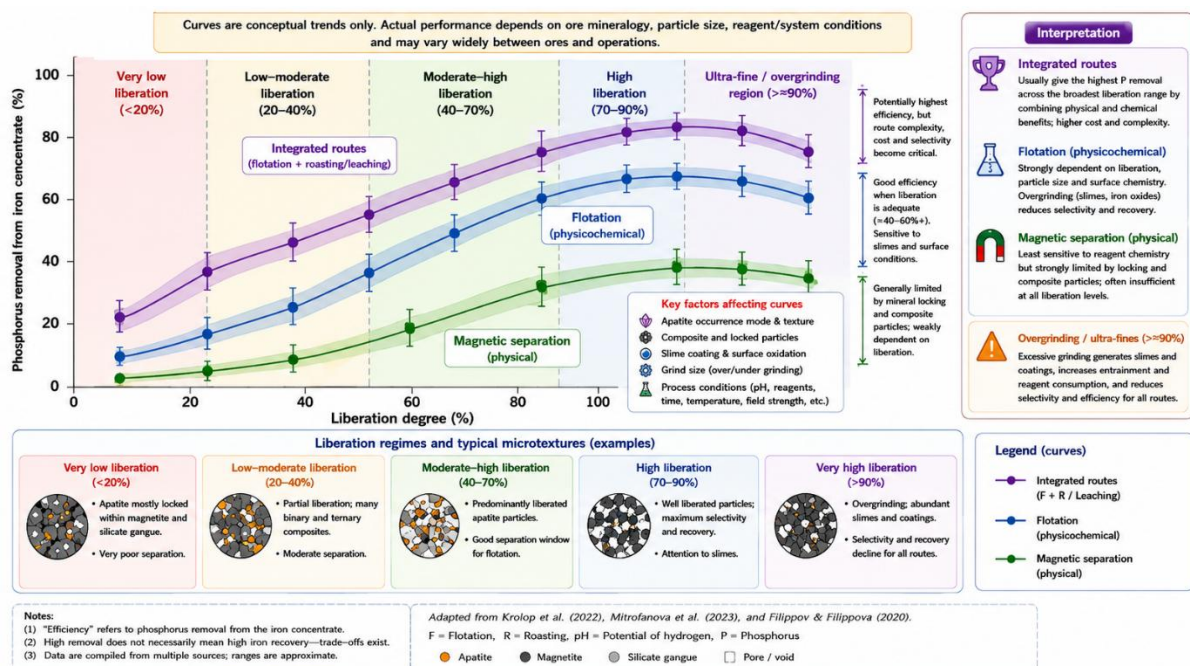


Figure 3. Conceptual relationship between liberation degree and phosphorus-removal efficiency for magnetic separation, flotation, and integrated beneficiation routes in apatite–magnetite iron ores. Adapted from Krolop et al. (2022), Mitrofanova et al. (2023), and Filippov and Filippova (2020).

Figure 3 shows flotation and integrated beneficiation generally achieve higher phosphorus removal over wider liberation ranges than magnetic separation. However, all are limited when apatite appears as ultrafine inclusions or composite particles. Excessive grinding improves liberation but lowers selectivity due to slime and surface coating. Therefore, optimizing beneficiation involves balancing liberation efficiency with operational challenges of ultrafine grinding.

Table 2 summarizes representative relationships among liberation size, phosphorus-removal performance, iron recovery, and major beneficiation limitations reported across different ore textures and occurrence modes.

Table 2. Relationship among liberation size, phosphorus-removal efficiency, iron recovery, and beneficiation limitations for different phosphorus occurrence modes in magnetite-bearing iron ores. Adapted from Krolop et al. (2022), Mitrofanova et al. (2023), Ivanyuk et al. (2016), Donskoi et al. (2022), and Filippov and Filippova (2020).

Ore type	Typical liberation size ( $\mu\text{m}$ )	P removal (%)	Fe recovery (%)	Main limitation
Coarse apatite associated with gangue	75–150	70–95	85–95	Moderate grinding demand
Fine apatite–magnetite intergrowth	20–75	40–75	70–90	Composite particles
Apatite inclusions in magnetite	<20–30	20–60	60–85	Ultrafine grinding requirement
Oolitic high-phosphorus iron ores	<10–20	50–90	50–80	Complex multiphase texture
Integrated flotation–leaching systems	Variable	70–98	75–92	High reagent and CAPEX demand

The relationships summarized in Table 2 reinforce that beneficiation performance is fundamentally governed by liberation behavior, mineralogical complexity, and particle associations rather than by phosphorus grade alone. These observations also explain why many laboratory-scale beneficiation studies report high phosphorus-removal efficiencies under highly controlled grinding conditions that are difficult to replicate at the industrial scale.

### 3.2. Mineralogical Constraints on Flotation Selectivity

Flotation selectivity in phosphorus-bearing magnetite ores is strongly controlled by mineralogical characteristics, surface chemistry, liberation behavior, and gangue composition. Although flotation remains the dominant method for selective apatite removal, its performance varies substantially with apatite dissemination mode, gangue mineralogy, particle-size distribution, and surface heterogeneity. Consequently, flotation efficiency cannot be generalized solely on the basis of reagent chemistry, as mineralogical variability frequently governs collector adsorption, froth selectivity, and entrainment behavior (Nikolenko & Doroshkevich, 2017).

Apatite dissemination is one of the most important constraints on flotation selectivity. Coarse, liberated apatite grains generally respond favorably to collector adsorption because sufficient apatite surface is exposed for interaction with fatty acids, hydroxamates, or mixed collector systems. In contrast, ultrafine apatite disseminations and binary apatite–magnetite intergrowths significantly reduce flotation selectivity because collector adsorption occurs simultaneously on partially exposed iron oxide and gangue surfaces. Under these conditions,

flotation recovery often increases at the expense of concentrate contamination and reagent consumption (Nie et al., 2017; Li et al., 2025a).

Gangue mineralogy also strongly influences flotation behavior. Amphibole- and pyroxene-rich, and mica-bearing gangue systems often exhibit elevated reagent demand because silicate minerals compete for collector adsorption and alter pulp rheology. In addition, some iron-bearing silicates may show weak surface reactivity toward anionic collectors, thereby reducing flotation selectivity and increasing entrainment of gangue particles into the froth phase (Prokopyev et al., 2018).

Another important issue concerns  $\text{Ca}^{2+}$  activation and the presence of dissolved ionic species. Calcium ions released from apatite dissolution or from recirculating process water may adsorb to gangue surfaces, promoting unintended collector adsorption. This effect is particularly significant under alkaline flotation conditions with fatty-acid collectors, as dissolved calcium species can alter electrostatic interactions and surface hydrophobicity. Consequently, flotation performance may vary substantially with water chemistry and recirculation conditions (Rodriguez-Mustafa et al., 2020; Salazar et al., 2020).

Slime coating is another major operational limitation in apatite flotation systems. Ultrafine iron oxides, clays, and silicate slimes can coat apatite surfaces, reducing collector adsorption efficiency and increasing reagent consumption. Slime coating also promotes froth instability and non-selective entrainment, particularly in ultrafine grinding environments. Excessive comminution may therefore simultaneously improve liberation and reduce flotation selectivity by increasing slime generation (Sparrow et al., 2022).

Surface heterogeneity further complicates flotation performance because apatite-bearing particles frequently exhibit mixed exposed surfaces that include magnetite, silicates, secondary alteration phases, and oxidation products. As a result, flotation response may vary substantially even among particles with similar bulk mineralogical composition. Several investigations using SEM-EDS mapping and automated mineralogy have shown that flotation selectivity correlates more strongly with the distribution of exposed surfaces than with bulk mineral abundance alone (Suleimen et al., 2025a).

Table 3 summarizes the key mineralogical constraints that affect flotation selectivity in phosphorus-bearing magnetite ores.

Table 3. Principal mineralogical constraints affecting flotation selectivity in phosphorus-bearing magnetite ores and their operational consequences. Adapted from Filippov and Filippova (2020), Krolop et al. (2022), Mitrofanova et al. (2023), and Donskoi et al. (2022)

Mineralogical feature	Flotation consequence
Fine apatite dissemination	Poor selectivity and composite particle recovery
Binary apatite–magnetite intergrowth	Increased entrainment and concentrated contamination
Amphibole-rich gangue	Elevated reagent consumption
Slime coating	Collector adsorption loss and froth instability
Surface oxidation	Reduced collector selectivity
Ca <sup>2+</sup> activation	Non-selective gangue flotation
Ultrafine iron oxides	Increased slime generation and entrainment

Figure 4 schematically illustrates the relationships between mineralogical characteristics and the flotation response of phosphorus-bearing magnetite ores.

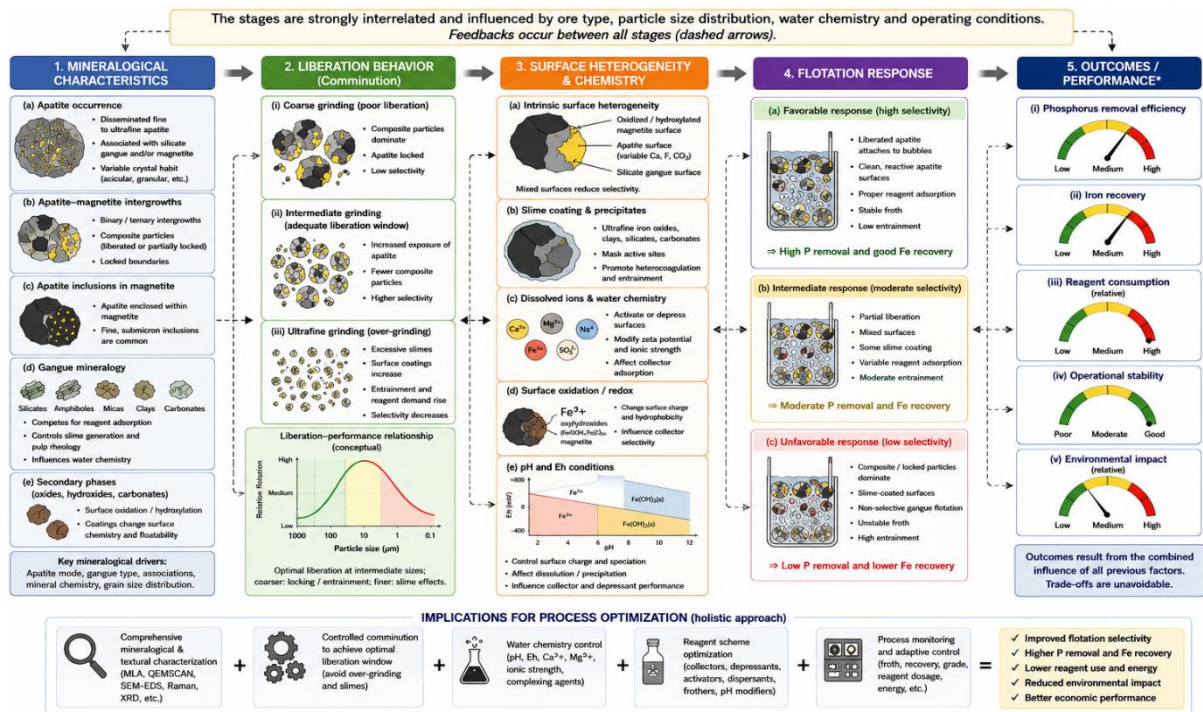


Figure 4. Conceptual framework relating mineralogical characteristics, liberation behavior, surface heterogeneity, and flotation response in apatite–magnetite beneficiation systems. Adapted from Filippov and Filippova (2020), Mitrofanova et al. (2023), Krolop et al. (2022), and Donskoi et al. (2022).

The relationships summarized in Table 3 and Figure 4 show that flotation selectivity is fundamentally governed by interactions among mineralogical texture, liberation behavior, surface chemistry, and particle-size distribution. Consequently, successful flotation optimization requires integrated control of comminution, reagent chemistry, water management, and process mineralogy, rather than isolated adjustment of flotation parameters alone.

The mineralogical and liberation constraints discussed in this section directly influence the beneficiation performance of the physical, physicochemical, thermal, and integrated dephosphorization routes covered in the following sections.

#### **4. Physical Separation Routes**

Physical beneficiation routes constitute the first stage of phosphorus removal in most magnetite iron ore processing circuits because they exploit differences in magnetic susceptibility, density, particle size, and surface properties between iron-bearing minerals and phosphorus-bearing gangue phases. Magnetic separation remains the dominant industrial technology for magnetite concentration due to its relatively low operating costs, high throughput, and mature industrial implementation. However, the effectiveness of physical separation for phosphorus removal strongly depends on liberation behavior and mineralogical associations (Suleimen et al., 2025b).

Low-intensity magnetic separation (LIMS) is widely used to recover magnetite from gangue minerals because magnetite is strongly ferromagnetic. By contrast, phosphorus-bearing minerals such as apatite are generally weakly magnetic or nonmagnetic. In ores where apatite occurs as liberated grains, magnetic separation may partially reject phosphorus-bearing particles during concentration. Birinci (2021) reported that combined magnetic separation and flotation routes improved the upgrading performance of apatite-bearing iron ore under favorable liberation conditions.

The main limitation of magnetic separation arises when apatite occurs as inclusions or fine intergrowths within magnetite-rich particles. Under these conditions, magnetic separation concentrates composite particles containing magnetite, thereby increasing the phosphorus content of the final concentrate. Similar limitations were observed in studies of Australian iron ore fines and Per Geijer iron oxide-apatite systems (Donskoi et al., 2022; Krolop et al., 2022). In many refractory ores, increasing grinding intensity improves liberation but also increases slime generation and the production of ultrafine particles.

Gravity separation has also been investigated for phosphorus-bearing iron ores, particularly in systems with density differences between iron-bearing minerals and gangue. Spirals, shaking tables, and dense media systems can achieve partial phosphorus rejection under coarse-particle conditions. However, gravity separation generally shows lower

selectivity for fine-grained apatite. Fine-particle entrainment, narrow density contrasts, and composite particle formation frequently reduce beneficiation efficiency.

Particle size distribution strongly affects physical separation performance. Coarse grinding often leaves particles locked, limiting phosphorus rejection. Conversely, ultrafine grinding increases surface area, slime coating, and particle aggregation. Slime generation is particularly problematic in downstream flotation because ultrafine iron oxide particles consume reagents, reducing selectivity. Several studies of oolitic high-phosphorus ores have shown that increasing liberation through fine grinding often yields diminishing returns because iron recovery decreases substantially at very fine particle sizes (Tang et al., 2016; Xiao & Zhou, 2019).

Table 4 compares the performance of physical beneficiation routes for phosphorus removal from magnetite iron ores under different operating conditions.

Table 4. Performance of physical beneficiation routes for phosphorus removal from magnetitic ores. Adapted from Tang et al. (2016), Birinci (2021), Donskoi et al. (2022), and Xiao and Zhou (2019).

Route	Typical P removal (%)	Fe recovery (%)	Main limitation
Magnetic separation	10–45	70–95	Composite particles
Gravity separation	5–30	60–85	Fine dissemination
Magnetic separation + grinding	25–60	50–85	Slime generation
Roasting + magnetic separation	40–80	65–92	Energy consumption

The data in Table 4 show that the efficiency of physical beneficiation depends strongly on ore texture and particle liberation. Magnetic separation alone rarely achieves sufficiently low phosphorus levels in ores with finely disseminated apatite. Additional grinding may improve liberation, but also increases operational complexity and iron losses.

Figure 5 illustrates the relationship between mineral liberation and phosphorus removal efficiency in physical beneficiation.

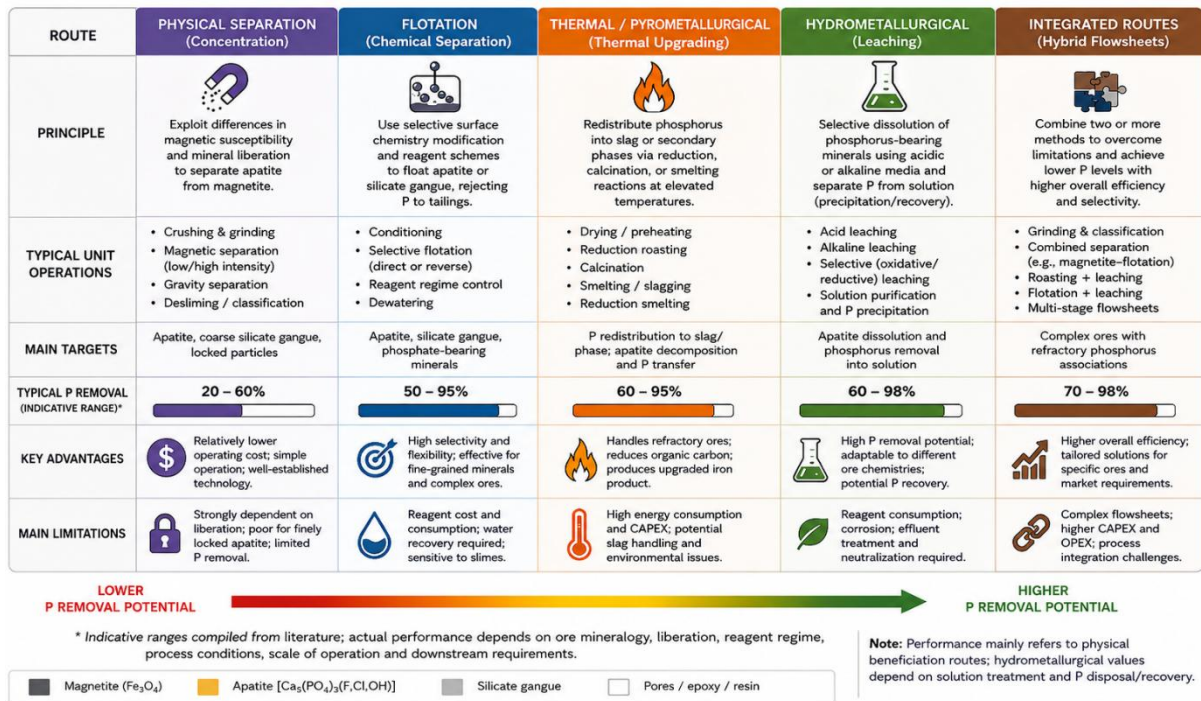


Figure 5. Influence of mineral liberation on phosphorus removal efficiency during physical separation. Adapted from Krolop et al. (2022), Donskoi et al. (2022), and Yu et al. (2026).

Figure 5 shows that improvements in liberation do not necessarily translate into proportional gains in beneficiation. Beyond a certain grinding threshold, slime generation and ultrafine particle formation can offset the benefits of liberation. Consequently, optimized grinding strategies must balance liberation, energy consumption, iron recovery, and downstream flotation performance. These limitations explain why flotation chemistry has become increasingly important for phosphorus removal from complex magnetitic ores, as discussed in the following section.

## 5. Flotation Chemistry and Surface Interactions

Flotation remains one of the most studied and industrially relevant methods for removing phosphorus from magnetite iron ores because apatite surface properties differ substantially from those of iron oxides under controlled chemical conditions. Selective flotation aims to separate phosphorus-bearing minerals from magnetite concentrates by using collectors, depressants, pH modifiers, dispersants, and water chemistry control. Nevertheless, flotation performance remains strongly dependent on mineral liberation, particle size distribution, and surface contamination.

Direct flotation of apatite typically involves the adsorption of anionic collectors onto the surfaces of phosphate minerals under alkaline conditions. Fatty acids are among the most commonly used collector classes because they selectively interact with calcium-bearing apatite surfaces. Hydroxamate collectors have also attracted considerable attention for their stronger selectivity and adsorption behavior in complex mineral systems. Derqaoui et al. (2022) and Ruan et al. (2019) demonstrated that collector selection substantially affects flotation efficiency, reagent consumption, froth stability, and selectivity.

Reverse flotation routes have also been investigated for dephosphorizing magnetite concentrates. In these systems, iron-bearing minerals are depressed while phosphorus-bearing minerals are floated. Starch remains one of the most widely used depressants for magnetite and hematite because it adsorbs to iron oxide surfaces, thereby suppressing flotation. Yehia et al. (2021) investigated fungal cellulase as a green alternative depressant for the reverse anionic flotation of high-phosphorus iron ores and observed improved selectivity under controlled conditions.

Despite extensive reagent development, flotation performance remains limited in ores with fine apatite dissemination and complex intergrowth textures. Iron oxide coatings on apatite surfaces reduce collector adsorption and lower selectivity. Slime coating further complicates flotation by causing ultrafine iron particles to adhere to apatite surfaces, altering flotation behavior and increasing reagent consumption. Similar problems occur in ores with high concentrations of clays and alteration products.

Water chemistry impacts flotation by affecting collector adsorption, zeta potential, and froth. Recirculating process water worsens instability due to dissolved ion buildup, especially in water-constrained industrial operations.

Another important limitation concerns the discrepancy between laboratory flotation performance and industrial-scale beneficiation behavior. Laboratory studies often use highly controlled reagent dosages, particle-size distributions, and pulp conditions that are difficult to maintain in industrial operations. Consequently, flotation selectivity often decreases under variable ore-feed conditions.

Table 5 summarizes the principal flotation reagents used for phosphorus removal from magnetite iron ores and their operational limitations.

Table 5. Main flotation reagents used for phosphorus removal from magnetitic iron ores and their operational limitations. Adapted from Ruan et al. (2019), Derqaoui et al. (2022), Silva (2020), and Yehia et al. (2021).

Reagent class	Typical function	Main advantage	Main limitation
Fatty acids	Apatite collector	Low cost	Poor selectivity
Hydroxamates	Selective collector	Improved apatite selectivity	Higher cost
Starch	Iron oxide depressant	Strong depression	Sensitive to dosage
Modified polymers	Surface modifier	Improved dispersion	Industrial complexity
Bio-depressants	Green depressants	Lower environmental impact	Limited industrial validation

Table 5 shows no reagent system is universally selective for all phosphorus-bearing iron ores. Reagent performance depends on mineral texture, water chemistry, and particle size, so optimization must be tailored to specific ore characteristics.

Figure 6 schematically illustrates the key surface interactions that govern selective flotation between apatite and magnetite particles.

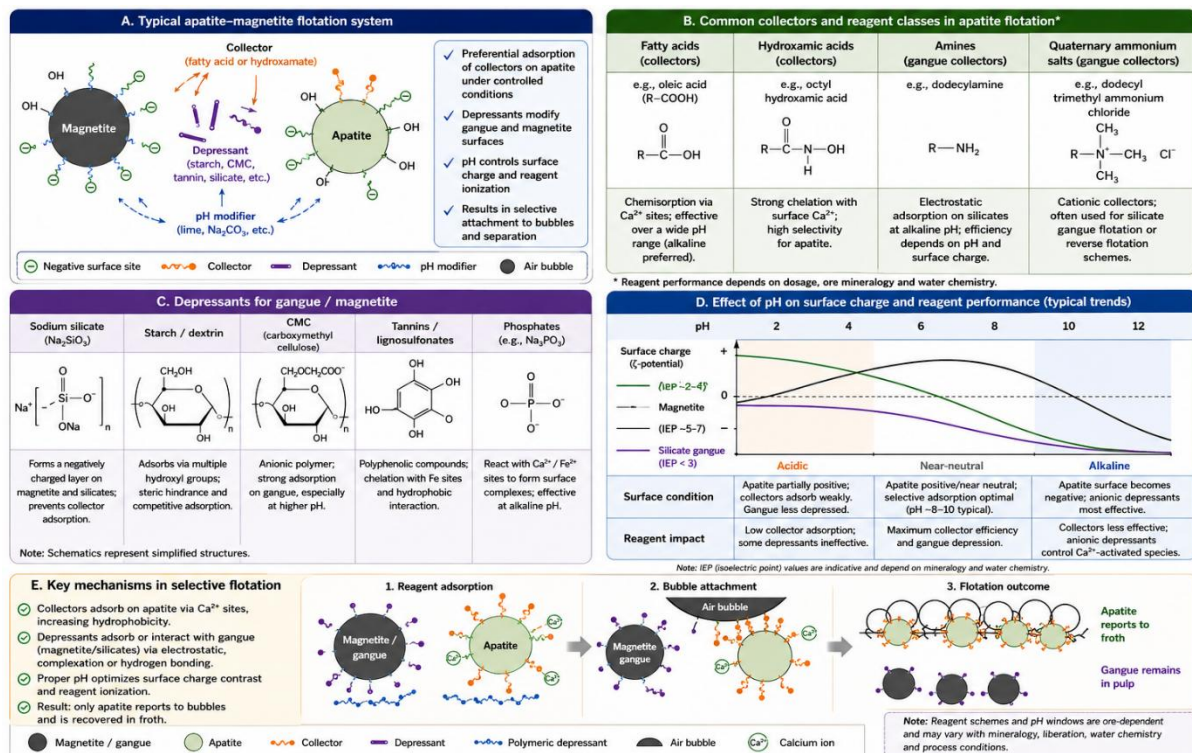


Figure 6. Surface-chemistry interactions during selective flotation of apatite and magnetite. Adapted from Ruan et al. (2019), Derqaoui et al. (2022), and Yehia et al. (2021).

The mechanisms shown in Figure 6 demonstrate that flotation selectivity depends on a delicate balance among collector adsorption, depressant coverage, electrostatic interactions, and particle surface contamination. Even small changes in pulp chemistry can substantially

alter flotation behavior. These limitations explain why flotation alone often fails to achieve sufficiently low phosphorus concentrations in refractory ores with fine intergrowths and composite particles.

The operational limitations of flotation have spurred growing interest in thermal and thermochemical beneficiation methods that can modify phosphorus distribution and improve downstream separation performance. These approaches are discussed in the next section.

## 6. Thermal and Thermochemical Approaches

Thermal and thermochemical beneficiation routes have attracted growing attention for treating refractory phosphorus-bearing iron ores because they modify mineral phases, phosphorus distribution, reduction behavior, and magnetic properties. These approaches often involve calcination, reduction roasting, smelting separation, alkaline treatment, or combined roasting-leaching systems to improve phosphorus liberation and downstream separation efficiency.

Reduction roasting followed by magnetic separation is one of the most extensively studied thermochemical routes for high-phosphorus iron ores. During roasting, iron oxides undergo phase transformations and reduction, producing metallic iron or magnetite, which can then be recovered by magnetic separation. Simultaneously, phosphorus-bearing minerals may redistribute, form slag, or selectively partition into nonmagnetic phases. Tang et al. (2016) demonstrated that direct reduction followed by melting separation improved phosphorus removal from high-phosphorus hematite systems under controlled temperature conditions.

The effectiveness of thermochemical routes depends strongly on roasting temperature, residence time, reducing atmosphere, additive selection, and mineralogical composition. Wu et al. (2021) observed that additives significantly affect reduction kinetics, iron grain growth, and phosphorus partitioning during the reduction roasting of refractory high-phosphorus ores. Similar observations were reported by Hu et al. (2025c), who demonstrated that the addition of  $\text{CaCO}_3$  promoted iron grain growth and enhanced phosphorus separation efficiency.

Calcination may also enhance beneficiation performance by altering the apatite structure and weakening mineral associations. Microwave-assisted heating has been investigated to selectively induce thermal stress and enhance liberation of iron-bearing minerals from phosphorus-bearing gangue phases. Cai et al. (2018) reported that combining

microwave processing with acid leaching improved selective liberation in high-phosphorus oolitic hematite systems.

Despite promising laboratory results, thermochemical beneficiation routes remain constrained by high energy intensity and operational complexity. Roasting temperatures often exceed 800–1200 °C, leading to substantial fuel consumption and increased greenhouse gas emissions. Additional concerns include refractory wear, process gas handling, and phosphorus redistribution into secondary phases, which may complicate downstream processing (Wu et al., 2021).

Another important issue is the discrepancy between laboratory-scale roasting experiments and industrial implementation. Many laboratory investigations use finely ground materials, highly controlled atmospheres, and long residence times that may not be economically feasible in industrial settings. Pilot-scale investigations remain relatively scarce, although some recent studies using rotary kilns and suspension roasting systems have demonstrated promising scalability (You et al., 2024; Zhang et al., 2023).

Table 6 compares the principal thermal and thermochemical routes proposed for removing phosphorus from magnetite and high-phosphorus iron ores.

Table 6. Thermal and thermochemical phosphorus-removal routes applied to magnetitic ores. Adapted from Tang et al. (2016), Cai et al. (2018), Wu et al. (2021), and Hu et al. (2025a).

Route	Typical temperature (°C)	Main mechanism	Principal limitation
Reduction roasting	800–1200	Iron reduction and phase transformation	Energy consumption
Calcination	600–1000	Mineral weakening and liberation	Limited selectivity
Smelting separation	>1300	Phosphorus partition into slag	High CAPEX
Microwave-assisted treatment	400–900	Selective thermal stress	Scale-up uncertainty
Roasting + leaching	700–1100	Enhanced phosphorus dissolution	Process complexity

Table 6 shows that thermochemical beneficiation can significantly enhance phosphorus removal from refractory ores, but often needs high temperatures, multiple steps, or harsh chemicals. This keeps energy use and costs high, hindering large-scale use.

Figure 7 schematically illustrates the key thermochemical mechanisms responsible for phosphorus redistribution during high-temperature treatment.

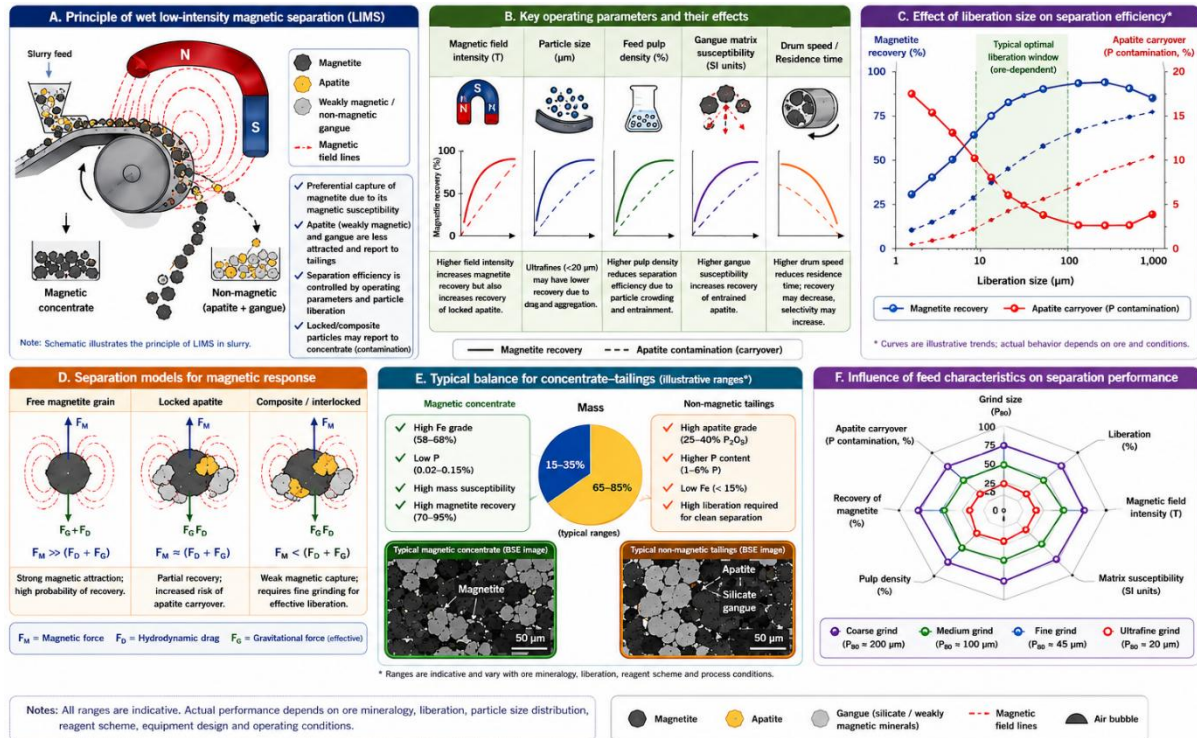


Figure 7. Simplified thermochemical pathways for phosphorus redistribution during high-temperature treatment. Adapted from Tang et al. (2016), Wu et al. (2023c), and Zhao et al. (2024).

Figure 7 shows that phosphorus behavior during thermochemical treatment depends strongly on the reduction atmosphere, slag chemistry, additive selection, and mineralogical texture. In several systems, phosphorus migrates into slag phases during smelting separation. In others, phosphorus remains partially associated with metallic iron, thereby limiting the efficiency of dephosphorization. These limitations have spurred growing interest in hydrometallurgical approaches that selectively dissolve phosphorus-bearing phases under milder conditions.

## 7. Hydrometallurgical Dephosphorization

Hydrometallurgical approaches have been investigated as alternatives or complementary methods for removing phosphorus from magnetite iron ores because selective dissolution can occur under controlled chemical conditions without the extreme temperatures associated with thermochemical beneficiation. Acid leaching, alkaline treatment, selective dissolution, and combined roasting-leaching systems have therefore attracted increasing attention, particularly for refractory ores with fine apatite dissemination.

Acid leaching is one of the most widely studied hydrometallurgical strategies. Hydrochloric, sulfuric, nitric, and organic acids have been evaluated for their ability to dissolve phosphorus-bearing phases selectively. The effectiveness of acid leaching depends strongly on acid concentration, temperature, residence time, particle-size distribution, and mineralogical texture. Pan et al. (2022) demonstrated that combining sodium magnetization roasting with acid and alkaline leaching improved phosphorus removal from high-phosphorus oolitic hematite ore.

Selective dissolution of apatite may occur under controlled conditions because phosphate minerals are often more soluble than magnetite and reduced iron phases. Nevertheless, iron co-dissolution remains a principal limitation of hydrometallurgical beneficiation. Excessive iron dissolution reduces iron recovery, increases reagent consumption, and complicates downstream solution treatment.

Effluent management is another major challenge in hydrometallurgical dephosphorization. Acid leaching produces phosphorus-rich effluents that contain dissolved iron, calcium, magnesium, aluminum, and other gangue species. Industrial implementation, therefore, requires neutralization systems, water treatment circuits, and reagent recycling strategies. Despite these requirements, many laboratory investigations offer limited discussion of wastewater treatment and environmental management.

Alkaline leaching has also been investigated because certain phosphorus-bearing phases dissolve selectively under alkaline conditions. Hu et al. (2025c) reported that combining high-pressure alkaline leaching with ultrasonic acid leaching improved impurity removal from refractory oolitic magnetite concentrates. However, these systems often involve elevated pressures, high reagent consumption, and operational complexity.

Another important issue concerns process economics. Although hydrometallurgical routes may achieve relatively high phosphorus removal efficiencies under laboratory conditions, industrial viability depends on reagent costs, acid consumption, solid-liquid separation efficiency, and effluent treatment requirements. Similar challenges are widely recognized in hydrometallurgical precipitation systems with complex multiphase suspensions (Pereira, 2026).

Table 7 summarizes the principal hydrometallurgical routes investigated for removing phosphorus from iron ores, along with their associated operational parameters.

Table 7. Hydrometallurgical phosphorus-removal systems and associated operational parameters. Adapted from Pan et al. (2022), Cai et al. (2018), Hu et al. (2025b), and Pereira (2026).

Route	Main reagent	Typical condition	Main limitation
HCl leaching	Hydrochloric acid	Ambient to 90 °C	Iron dissolution
H <sub>2</sub> SO <sub>4</sub> leaching	Sulfuric acid	Ambient to 100 °C	Effluent generation
Alkaline leaching	NaOH	Elevated pressure	Reagent cost
Roasting + leaching	Mixed systems	Multistage process	Process complexity
Ultrasonic-assisted leaching	Acid + ultrasound	Enhanced dissolution	Scale-up limitation

The hydrometallurgical systems summarized in Table 7 show that phosphorus removal efficiency often improves under aggressive chemical conditions. However, these gains are often accompanied by higher reagent consumption, greater operational complexity, and more demanding wastewater treatment requirements.

Figure 8 presents representative hydrometallurgical dephosphorization flowsheets proposed for refractory phosphorus-bearing iron ores.

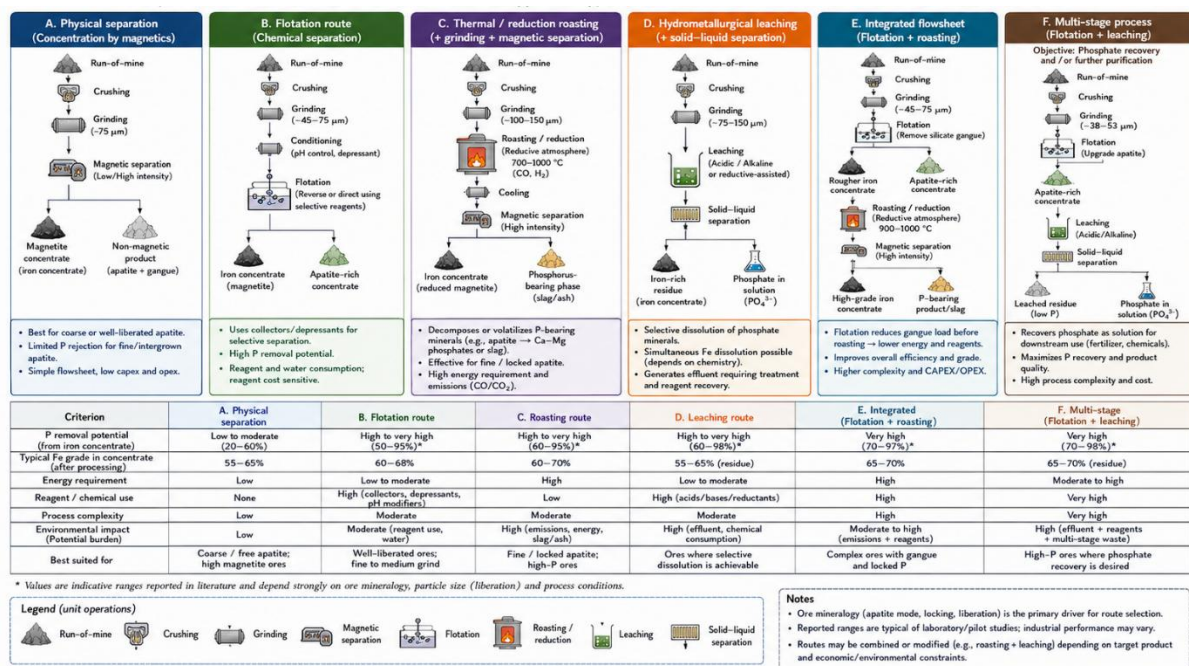


Figure 8. Simplified hydrometallurgical dephosphorization routes for magnetitic ores. Adapted from Pan et al. (2022), Hu et al. (2025a), and Pereira (2026).

The flowsheets in Figure 8 show that hydrometallurgical beneficiation rarely operates as an isolated process stage. Most proposed systems integrate grinding, roasting, leaching, washing, filtration, and neutralization. Consequently, process integration is increasingly important for improving overall beneficiation performance and reducing operational costs. These integrated beneficiation strategies are discussed in the following section.

## 8. Integrated Flowsheets and Process Integration

Integrated beneficiation flowsheets have emerged as one of the most promising approaches for treating refractory phosphorus-bearing magnetitic iron ores because no single beneficiation route consistently achieves both high phosphorus removal and high iron recovery across all mineralogical conditions. Current evidence suggests that integrated systems become increasingly necessary as ore texture, apatite dissemination, and the complexity of mineral locking increase. Nevertheless, integrated beneficiation should not be interpreted as a universally superior solution. In many cases, increasing flowsheet complexity improves metallurgical performance while reducing operational robustness, process flexibility, and economic attractiveness (Wang et al., 2026).

The effectiveness of integrated beneficiation depends strongly on the relationship between mineralogical occurrence and process-route compatibility. Ores with coarse, liberated apatite associated with silicate gangue may respond adequately to relatively simple circuits that use magnetic separation followed by flotation. In contrast, ultrafine apatite dissemination, binary apatite–magnetite intergrowths, and inclusion-type phosphorus occurrences frequently require multistage processing involving fine grinding, thermal modification, selective flotation, or hydrometallurgical treatment. Consequently, ore-dependent route selection becomes a critical factor in determining industrial applicability.

Magnetic separation combined with flotation remains one of the most extensively studied integrated approaches for phosphorus-bearing magnetite ores. In these systems, magnetic separation first concentrates iron-bearing minerals while rejecting part of the gangue. The magnetic concentrate then undergoes flotation to selectively remove apatite and other phosphorus-bearing phases. Xiao and Zhou (2019) reported that low-intensity magnetic separation followed by reverse flotation improved phosphorus reduction in magnetic-roasted, high-phosphorus oolitic iron ore. Similar integrated circuits have shown favorable performance in ores with partially liberated apatite, where magnetic concentration alone fails to meet acceptable phosphorus specifications.

Despite its industrial maturity, the magnetic separation–flotation route remains highly sensitive to liberation behavior and slime generation. Fine grinding may increase apatite exposure while also increasing ultrafine particle entrainment, reagent consumption, and froth instability. Industrial observations indicate that variability in water chemistry and dissolved ionic species frequently reduces flotation selectivity under recirculating process-water

conditions. Existing literature still overemphasizes laboratory flotation efficiencies obtained under highly controlled conditions while underestimating the operational instability associated with industrial-scale circuits.

Reduction roasting combined with magnetic separation and leaching has also attracted considerable attention, particularly for refractory oolitic iron ores and complex multiphase systems. These flowsheets aim to modify iron mineral phases during roasting while improving phosphorus liberation and selective dissolution. Pan et al. (2022) proposed a sodium magnetization roasting–magnetic separation–acid and alkaline leaching route that improves both iron recovery and phosphorus rejection. Thermal modification may partially overcome liberation limitations by destabilizing phosphorus-bearing associations and promoting selective partitioning.

The industrial use of roasting-based systems remains uncertain due to high energy use, process instability, refractory wear, gas treatment needs, and high CAPEX, which often negate laboratory-based benefits. Key challenges include maintaining thermal uniformity and stable phosphorus partitioning at large scales. Many studies rely on finely ground feeds, long residence times, and controlled atmospheres that are hard to replicate industrially.

Hydrometallurgical integration routes that combine leaching with flotation, roasting, or magnetic separation can achieve very high phosphorus-removal efficiencies. However, these systems introduce additional operational constraints, including reagent recycling, corrosion management, solid–liquid separation, and wastewater treatment. Selective phosphorus dissolution without excessive iron losses remains particularly challenging in complex magnetite–apatite systems. In several cases, high phosphorus-removal efficiencies are accompanied by substantial reagent demand and an increased environmental burden. This indicates that metallurgical performance alone should not be the primary criterion for route selection.

Integrated beneficiation routes often improve overall selectivity because different stages address distinct mineralogical and physicochemical limitations. Magnetic separation exploits magnetic susceptibility contrasts, flotation modifies surface chemistry, roasting alters mineral phases, and leaching promotes selective dissolution. However, greater process integration also increases interdependencies. Instabilities generated in one stage may propagate throughout the beneficiation circuit, reducing operational stability and increasing process control complexity.

Water management is crucial in integrated systems as recirculation can change flotation chemistry, increase dissolved ions, and alter collector adsorption. Roasting–leaching systems produce complex streams with phosphorus, iron, alkalis, sulfates, and solids. Industrial use needs integrated water treatment and reagent recovery for stability.

Ore variability is another major limitation that is often underestimated in the current literature. Integrated flowsheets optimized for one ore type may perform poorly when applied to ores with different textures, gangue compositions, liberation characteristics, or phosphorus occurrence modes. Consequently, successful industrial implementation increasingly depends on predictive geometallurgical characterization that integrates mineralogy, liberation behavior, process simulation, and operational control. Current evidence suggests that integrated beneficiation systems become increasingly dependent on accurate ore characterization as flowsheet complexity increases.

Table 8 compares representative integrated beneficiation flowsheets proposed for phosphorus-bearing magnetite iron ores.

Table 8. Comparative assessment of integrated phosphorus-removal flowsheets for magnetitic ores. Adapted from Xiao and Zhou (2019), Pan et al. (2022), Wu et al. (2023b), and Zhao et al. (2024).

Integrated route	Main advantage	Main limitation	Industrial maturity
Magnetic separation + flotation	Improved selectivity	Slime sensitivity	High
Roasting + magnetic separation	Enhanced liberation	Energy consumption	Moderate
Roasting + leaching	High phosphorus removal	Complex operation	Low to moderate
Smelting + slag separation	Deep dephosphorization	High CAPEX	Moderate
Hybrid multiprocess systems	Flexible operation	Process integration complexity	Emerging

The comparison summarized in Table 8 shows that integrated beneficiation systems generally achieve higher phosphorus-removal efficiencies than single-stage routes. However, these gains are often accompanied by higher CAPEX, greater operational complexity, higher energy consumption, and stricter process-control requirements. This trade-off is a principal barrier to the industrial implementation of highly integrated beneficiation circuits.

Figure 9 presents a representative integrated beneficiation flowsheet for refractory phosphorus-bearing magnetite iron ores.

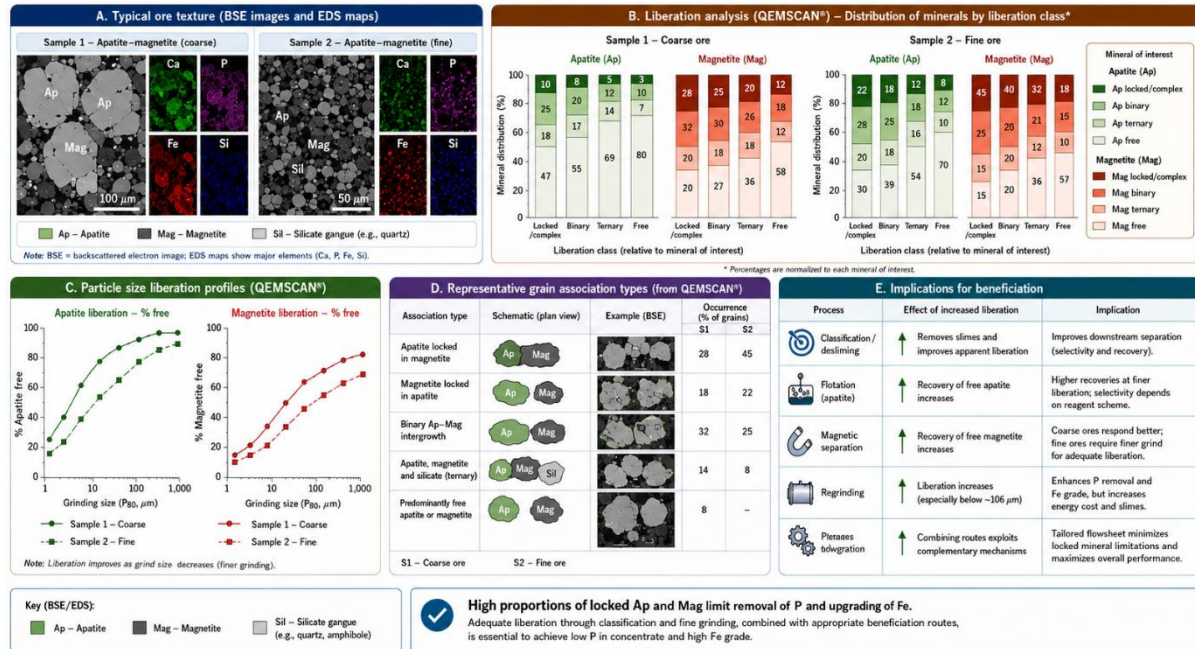


Figure 9. Typical integrated beneficiation flowsheet for phosphorus-bearing magnetitic ores. Adapted from Pan et al. (2022), Wu et al. (2023a), and Zhao et al. (2024).

The flowsheet in Figure 9 reflects the growing trend toward multiprocess beneficiation systems that integrate physical, chemical, and thermal operations. Current evidence indicates that future progress in phosphorus removal from refractory magnetite ores will likely depend on integrated geometallurgical frameworks rather than isolated beneficiation stages. Nevertheless, industrial scalability remains constrained by energy demand, process stability, ore variability, water management, and economic feasibility. These trade-offs are critically examined in the following section.

## 9. Comparative Analysis of Dephosphorization Routes

### 9.1. Comparative Beneficiation Performance

The comparative evaluation of phosphorus-removal technologies shows that beneficiation performance cannot be assessed solely by phosphorus-removal efficiency. Iron recovery, concentrate grade, liberation behavior, operational stability, energy demand, reagent consumption, scalability, and environmental burden must also be considered when selecting a dephosphorization strategy for magnetite-bearing iron ores. Current evidence suggests that ore

mineralogy and the mode of phosphorus occurrence exert a stronger influence on beneficiation response than bulk phosphorus concentration alone.

No single dephosphorization route is universally optimal for all phosphorus-bearing magnetite ores. Beneficiation performance varies substantially with apatite dissemination, mineral locking, gangue composition, particle texture, and ore genesis. Ores with coarse, liberated apatite associated with silicate gangue generally respond well to conventional flotation and magnetic separation circuits. In contrast, ultrafine apatite dissemination, binary apatite–magnetite intergrowths, and inclusion-type phosphorus occurrences frequently require integrated beneficiation routes that involve fine grinding, selective flotation, thermal modification, or hydrometallurgical treatment.

Magnetic separation remains the most industrially mature beneficiation route because of its relatively low operating costs, high throughput, and compatibility with conventional magnetite concentration circuits. Low-intensity magnetic separation (LIMS), wet high-intensity magnetic separation (WHIMS), and high-gradient magnetic separation (HGMS) are widely used in industrial operations. However, magnetic separation alone rarely achieves sufficiently low phosphorus concentrations in ores with ultrafine apatite dissemination or complex composite particles. This limitation is particularly severe in Kiruna-type and IOCG-related systems, where apatite frequently occurs as fine inclusions within magnetite-rich particles.

Flotation remains the dominant physicochemical approach for selective phosphorus removal because apatite surface properties can be manipulated through reagent chemistry, pH adjustment, depressant systems, and pulp conditioning. Under favorable liberation conditions, flotation systems can achieve phosphorus-removal efficiencies of 70–90%. Nevertheless, flotation selectivity deteriorates substantially in ores with slime coating, ultrafine dissemination, surface oxidation, or strong mineralogical heterogeneity. Industrial observations indicate that variability in water chemistry and dissolved ionic species strongly affect collector adsorption and froth stability. Existing literature often overemphasizes laboratory flotation performance while underestimating the operational instability associated with recirculating process water and the entrainment of ultrafine particles.

Thermal and thermochemical routes often achieve deeper dephosphorization because high-temperature treatment alters mineral phases and destabilizes phosphorus-bearing associations. Reduction roasting followed by magnetic separation has shown promising results

for refractory oolitic iron ores, where liberation-based beneficiation alone is insufficient. However, industrial applicability remains questionable in many cases because roasting systems require elevated energy inputs, refractory maintenance, gas-treatment infrastructure, and strict thermal process control. These limitations substantially increase CAPEX and operational complexity.

Hydrometallurgical routes may partially overcome liberation constraints through selective dissolution. Acidic and alkaline leaching systems have demonstrated high phosphorus-removal efficiencies in several laboratory investigations. However, maintaining selective phosphorus dissolution without excessive iron losses remains a major unresolved challenge. Industrial implementation is also constrained by acid consumption, corrosion management, reagent recycling, and wastewater treatment. Some hydrometallurgical systems may therefore become environmentally unfavorable despite high phosphorus-removal efficiency.

Integrated beneficiation systems that combine flotation, magnetic separation, roasting, and/or hydrometallurgical treatment generally deliver the highest overall metallurgical performance by addressing multiple mineralogical constraints simultaneously. These systems improve control over liberation behavior, composite particles, and selective phosphorus removal. However, integrated flowsheets require advanced process control, detailed geometallurgical characterization, and stable ore-feed predictability. Industrial implementation, therefore, depends strongly on managing ore variability and ensuring long-term operational robustness.

Table 9 critically compares the principal phosphorus-removal technologies according to beneficiation performance, operational complexity, and industrial applicability.

Table 9. Comparative analysis of phosphorus-removal technologies for magnetitic iron ores. Adapted from Pereira and Papini (2015), Tang et al. (2016), Pan et al. (2022), and Yu et al. (2026).

Route	Typical P removal (%)	Iron recovery (%)	Relative energy demand	Industrial maturity	Main limitation
Magnetic separation	20–60	70–95	Low	Very high	Liberation dependency
Flotation	50–90	70–92	Moderate	High	Slime sensitivity and reagent demand
Reduction roasting	60–95	65–90	High	Moderate	Energy consumption and gas treatment

Hydrometallurgy	60–98	60–85	Moderate to high	Low to moderate	Effluent treatment and reagent recycling
Integrated systems	70–98	75–95	High	Emerging	Operational complexity

The comparison in Table 9 shows that no single beneficiation route simultaneously maximizes phosphorus removal, iron recovery, operational simplicity, and economic feasibility. Therefore, route selection must consider mineralogical texture, ore variability, infrastructure availability, environmental constraints, and process integration requirements, rather than focusing exclusively on phosphorus removal efficiency.

Figure 10 schematically illustrates the trade-offs among phosphorus removal efficiency, iron recovery, and process complexity across the principal beneficiation routes.

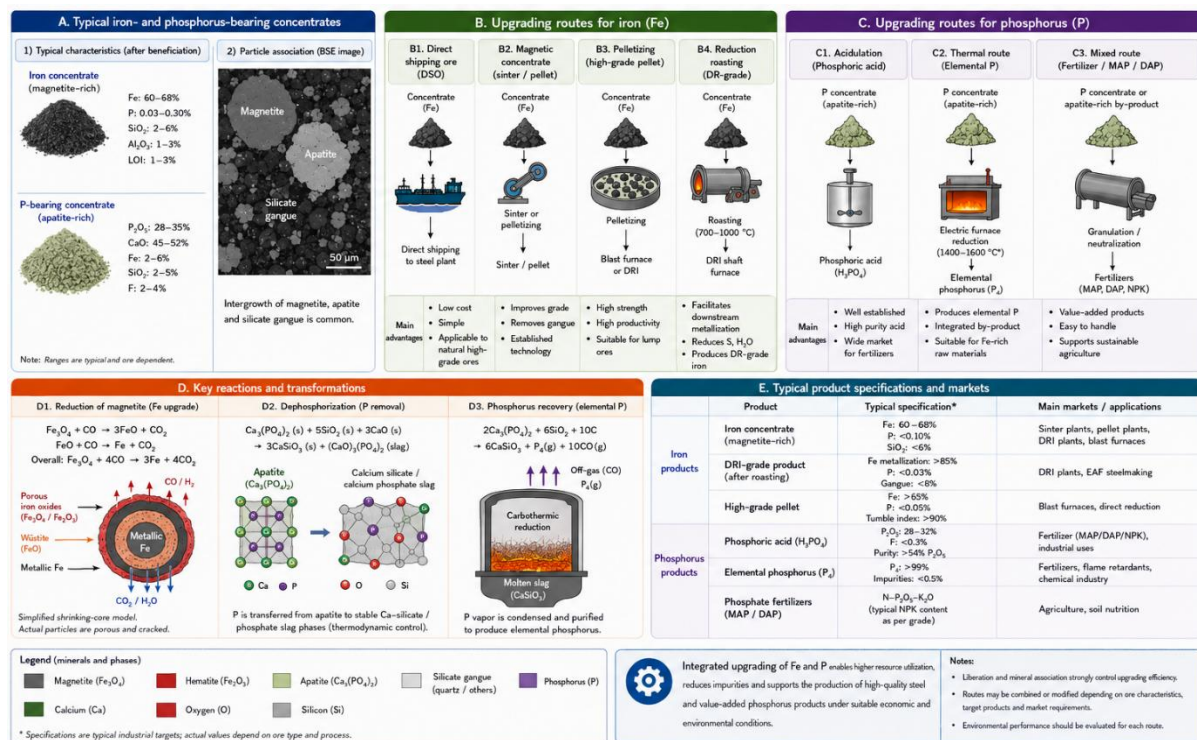


Figure 10. Trade-off relationship between phosphorus removal efficiency, iron recovery, and process complexity. Adapted from Pereira and Papini (2015), Pan et al. (2022), and Xu et al. (2025).

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Thermal and thermochemical routes often achieve deeper dephosphorization because high-temperature treatment alters mineral phases and destabilizes phosphorus-bearing associations. Reduction roasting followed by magnetic separation has shown promising results

for refractory oolitic iron ores, where liberation-based beneficiation alone is insufficient. However, industrial applicability remains questionable in many cases because roasting systems require elevated energy inputs, refractory maintenance, gas-treatment infrastructure, and strict thermal process control. These limitations substantially increase CAPEX and operational complexity.

Hydrometallurgical routes can partially overcome liberation constraints via selective dissolution. Acidic and alkaline leaching achieve high phosphorus removal in the lab, but avoiding iron loss while maintaining selectivity remains difficult. Industrial use faces issues like acid use, corrosion, reagent recycling, and wastewater treatment. Consequently, some systems may be environmentally unfriendly despite effective phosphorus removal.

Integrated beneficiation systems that combine flotation, magnetic separation, roasting, and/or hydrometallurgical treatment generally deliver the highest overall metallurgical performance by addressing multiple mineralogical constraints simultaneously. These systems improve control over liberation behavior, composite particles, and selective phosphorus removal. However, integrated flowsheets require advanced process control, detailed geometallurgical characterization, and stable ore-feed predictability. Industrial implementation, therefore, depends strongly on ore-variability management and long-term operational robustness.

## **9.2. Operational Trade-Offs and Process Constraints**

Operational trade-offs are a principal barrier to industrial dephosphorization of magnetite-bearing iron ores. Although many beneficiation routes achieve promising phosphorus-removal efficiencies under controlled laboratory conditions, industrial implementation is often constrained by energy demand, liberation requirements, process complexity, water management, and operational reproducibility.

Energy demand varies across beneficiation routes. Magnetic separation has the lowest energy consumption, relying on differences in magnetic susceptibility, but ultrafine apatite inclusions can increase grinding energy. Flotation needs moderate energy for grinding, conditioning, aeration, and pumping. Roasting and smelting systems require the most energy due to process temperatures of 800–1300 °C.

Liberation dependency is another critical operational limitation. Coarse apatite associated with gangue minerals may be liberated under relatively moderate grinding

conditions. In contrast, ultrafine apatite dissemination and complex intergrowth textures require aggressive comminution. Excessive grinding may improve liberation while simultaneously increasing slime generation, reagent consumption, and entrainment losses. Current evidence suggests that beneficiation performance often reaches an optimal liberation window rather than continuously improving as particle size decreases.

Selectivity versus recovery trade-offs also become increasingly important under industrial conditions. High phosphorus removal may require fine grinding and aggressive reagent schemes, which can simultaneously reduce iron recovery due to entrainment and slime generation. Similarly, increased collector dosage may improve apatite recovery while reducing flotation selectivity because gangue minerals and partially liberated particles are unintentionally recovered. This trade-off remains insufficiently discussed in many laboratory investigations.

Scale-up risk varies substantially across beneficiation routes. Flotation systems are particularly sensitive to variability in water chemistry, dissolved ionic species, and ultrafine slimes. Roasting systems face challenges with thermal uniformity, refractory degradation, and gas handling. Hydrometallurgical routes are strongly constrained by effluent management, reagent recycling, and corrosion control. Integrated beneficiation circuits pose additional operational risks because process stability depends on maintaining simultaneous control of multiple interconnected stages (Hu et al., 2025c).

Water management is a key industry challenge. Fine-particle flotation generates recirculating streams containing dissolved calcium, magnesium, and iron, as well as ultrafine slimes, which affect flotation selectivity, froth stability, and reproducibility. Hydrometallurgical systems add complexity due to the need for effluent treatment and reagent recycling to meet environmental compliance requirements.

Process complexity also increases substantially in integrated beneficiation systems. Multi-stage routes that combine grinding, magnetic separation, flotation, roasting, and leaching often deliver superior metallurgical performance but require advanced instrumentation, process automation, and detailed geometallurgical characterization. Industrial applicability, therefore, depends not only on metallurgical efficiency but also on operational robustness and adaptability to ore variability.

The operational constraints discussed above demonstrate that optimizing beneficiation must balance liberation efficiency, metallurgical selectivity, energy demand, environmental

burden, and long-term operational stability, rather than maximizing phosphorus removal efficiency alone.

### **9.3. Industrial Maturity and Economic Constraints of Dephosphorization Routes**

Although laboratory studies often report high phosphorus removal efficiencies under optimized conditions, industrial implementation depends heavily on technological maturity, scalability, CAPEX, OPEX, environmental burden, and operational robustness. Therefore, metallurgical performance alone cannot determine industrial feasibility.

Magnetic separation has the highest technological readiness level (TRL) because magnetic concentration circuits are already fully integrated into industrial magnetite beneficiation plants worldwide. These systems generally have low CAPEX and OPEX because they require relatively simple infrastructure and minimal reagent use. However, their industrial effectiveness remains fundamentally constrained by liberation behavior and mineral locking.

Flotation routes are highly mature, with apatite flotation systems established in phosphate and iron ore industries. However, flotation circuits need constant control of water chemistry, reagent dosage, froth stability, and particle size. Operating costs may rise significantly with fine particles due to higher reagent and water treatment needs (Hu et al., 2025a).

Thermal and thermochemical routes are less industrially mature despite the potential for refractory phosphorus ores. Reduction roasting needs high energy, gas infrastructure, refractory upkeep, and precise temperature control. The literature often reports high phosphorus removal but underestimates the economic costs of thermal processing. Consequently, the industrial viability of many roasting methods remains uncertain.

Hydrometallurgical routes are intermediate between lab potential and industrial use. While selective phosphorus dissolution can efficiently remove phosphorus, industrial applications face challenges such as high acid consumption, reagent recycling, wastewater treatment, corrosion, and solid–liquid separation, which increase costs and environmental complexity (Hu et al., 2025b).

Integrated beneficiation systems usually achieve the highest phosphorus-removal efficiencies by combining multiple mechanisms within a single flowsheet. However, they require more capital, are more operationally sensitive, and require strict process control.

Industrial use requires predictable geometallurgy and a stable ore feed, which is particularly difficult with deposits exhibiting strong mineralogical variability.

Figure 11 presents a conceptual comparison of the principal dephosphorization routes based on technological readiness level (TRL), CAPEX, phosphorus-removal potential, and environmental burden.

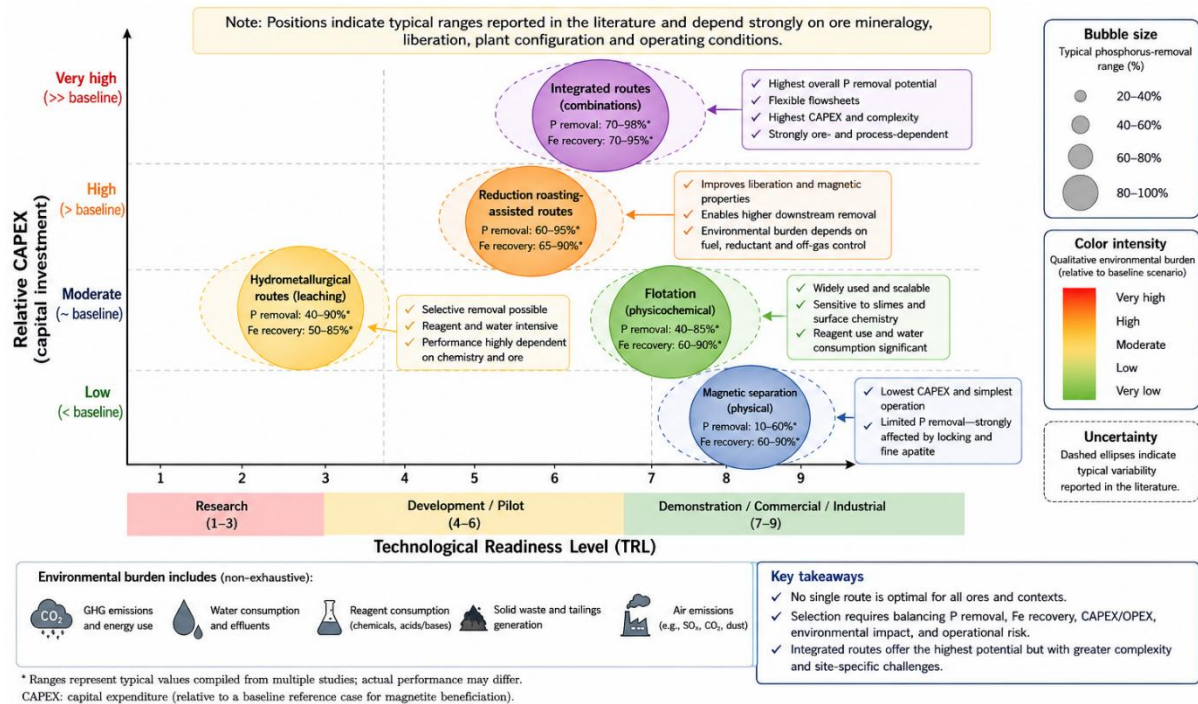


Figure 11. Conceptual relationship among technological readiness level (TRL), CAPEX, phosphorus-removal potential, and environmental burden for principal dephosphorization routes applied to magnetite-bearing iron ores. Bubble size represents typical phosphorus-removal potential, whereas color intensity qualitatively indicates relative environmental burden. Adapted from Pereira and Papini (2015), Tang et al. (2016), Pan et al. (2022), and Mitrofanova et al. (2023).

The framework in Figure 11 shows that the most efficient phosphorus-removal technologies are not always the most mature or eco-friendly. Magnetic separation has the highest TRL and is the simplest to operate. Conversely, roasting and integrated methods achieve deeper removal but with higher CAPEX, energy use, and environmental impact.

Table 10 summarizes the key relationships among industrial maturity, economic constraints, scalability, and environmental burden for the primary dephosphorization route.

Table 10. Comparative assessment of industrial maturity, economic constraints, scalability, and environmental burden for phosphorus-removal technologies applied to magnetite-bearing iron ores. Adapted from Pereira and Papini (2015), Tang et al. (2016), Filippov and Filippova (2020), Pan et al. (2022), and Mitrofanova et al. (2023).

Route	Typical TRL	Relative CAPEX	Relative OPEX	Scalability	Environmental burden	Main industrial limitation
Magnetic separation	8–9	Low	Low	Very high	Low	Liberation dependency
Flotation	7–9	Moderate	Moderate	High	Moderate	Slime generation and reagent demand
Reduction roasting	5–7	High	High	Moderate	High	Energy consumption and gas treatment
Hydrometallurgy	3–6	Moderate to high	High	Low to moderate	High	Effluent treatment and reagent recycling
Integrated routes	4–7	Very high	High	Moderate	Moderate to high	Operational complexity and process integration

The comparative relationships summarized in Table 10 indicate that deeper dephosphorization often requires greater process complexity, higher capital investment, and a stronger environmental-management infrastructure. Consequently, industrial route selection must balance metallurgical efficiency with operational feasibility and long-term economic sustainability.

#### 9.4. Sustainability and Industrial Implications

Sustainability considerations are increasingly important in phosphorus-removal strategies because routes with high metallurgical efficiency may also impose substantial environmental burdens, energy demand, and waste-management complexity. Industrial optimization should therefore consider greenhouse-gas emissions, water consumption, reagent recycling, tailings generation, and long-term operational stability alongside metallurgical performance.

Roasting and thermochemical systems generally impose the highest environmental burden due to elevated fuel consumption, CO<sub>2</sub> emissions, refractory wear, and gas-treatment requirements. Hydrometallurgical routes may also generate significant environmental impacts due to acid consumption, wastewater treatment, and the generation of secondary residues.

Magnetic separation systems generally exhibit lower environmental impact because they require minimal reagent use and relatively simple operational infrastructure.

Integrated beneficiation systems may improve overall sustainability when properly optimized because process integration enables better resource utilization, selective phosphorus removal, and improved metallurgical recovery. However, these systems also require advanced water management, reagent recycling, and process-control strategies to avoid excessive operational complexity.

A major unresolved challenge is the discrepancy between laboratory-scale beneficiation performance and real-world industrial operations. Many studies use highly selective feed samples, optimized reagent conditions, fresh process water, and aggressive grinding conditions that do not adequately represent industrial conditions. Reported phosphorus-removal efficiencies may therefore substantially overestimate real-world plant performance (Hosseini et al., 2022).

Several critical knowledge gaps remain underaddressed. Predictive liberation modeling remains limited for complex apatite–magnetite intergrowth systems. Industrial datasets that integrate process mineralogy, flotation chemistry, and long-term plant performance remain scarce. Furthermore, relatively few investigations combine geometallurgical variability analysis with process simulation and pilot-scale validation (Heidarian et al., 2016).

Future research should prioritize integrated process optimization, selective liberation, reagent-efficiency improvement, industrial water recirculation, and environmental-footprint reduction rather than exclusively pursuing maximum phosphorus-removal efficiency. Greater emphasis should also be placed on industrial reproducibility, pilot-scale validation, and ore-variability management to reduce the current gap between laboratory experimentation and industrial implementation.

## **10. Industrial Applications and Case Studies**

Industrial implementation of phosphorus-removal technologies remains far more limited than laboratory-scale experimentation. Although numerous beneficiation routes have demonstrated promising phosphorus-reduction efficiencies under controlled conditions, only a relatively small number of operations have achieved sustained industrial performance with acceptable operational stability and economic viability (Tornos et al., 2024).

China is a major region where phosphorus-bearing iron ores have spurred extensive beneficiation research, as several Chinese iron deposits host refractory oolitic ores with elevated phosphorus levels. Consequently, Chinese investigations place strong emphasis on reduction roasting, magnetic separation, flotation, and integrated thermochemical routes. Several pilot-scale studies using rotary kilns, suspension roasting systems, and gas-based reduction have demonstrated encouraging results under semi-industrial conditions (You et al., 2024; Zhao et al., 2024).

Australian high-phosphorus iron ore systems have also attracted considerable attention because phosphorus penalties substantially affect export value and steelmaking suitability. Donskoi et al. (2022) investigated ultrasonic treatment of high-phosphorus Australian iron ore fines and demonstrated that mineralogical texture strongly influences the beneficiation response. Nevertheless, large-scale industrial implementation remains constrained by process economics and ore variability.

Brazilian iron ore systems generally contain lower phosphorus concentrations than many Chinese oolitic ores. However, some itabiritic and magnetitic deposits exhibit localized phosphorus enrichment associated with apatite dissemination and gangue concentration. Pereira and Papini (2015) emphasized that beneficiation strategies must be tailored to the mode of phosphorus occurrence rather than generalized based on bulk chemistry alone.

Several studies of Kiruna-type and iron oxide-apatite systems in Sweden, Chile, Iran, and Russia focused primarily on mineralogical characterization, ore genesis, and apatite distribution rather than on direct industrial beneficiation. Nevertheless, these investigations provide critical insights into liberation behavior, apatite occurrence, and process mineralogy (La Cruz et al., 2020; Tornos et al., 2021; Pietruszka et al., 2023).

One of the major limitations of the current literature is the scarcity of long-term industrial operational data. Many publications report short-duration pilot tests or laboratory campaigns that omit discussion of equipment wear, reagent recirculation, water management, operational stability, or maintenance requirements. Consequently, the practical scalability of several proposed beneficiation routes remains uncertain.

Table 11 summarizes representative industrial and pilot-scale applications for the removal of phosphorus from magnetite and high-phosphorus iron ores.

Table 11. Reported industrial and pilot-scale applications for phosphorus removal from magnetic ores. Adapted from Donskoi et al. (2022), You et al. (2024), Zhao et al. (2024), and Pereira and Papini (2015).

Region	Ore type	Main beneficiation route	Scale	Main challenge
China	Oolitic iron ore	Roasting + magnetic separation	Pilot/industrial	Energy demand
Australia	High-P fines	Ultrasonic beneficiation	Pilot	Texture variability
Brazil	Itabirite/magnetitic ore	Magnetic separation + flotation	Industrial	Liberation variability
Sweden	IOA systems	Mineralogical assessment	Laboratory/pilot	Fine intergrowth
Russia	Apatite-magnetite ore	Integrated beneficiation	Pilot	Complex mineralogy

The industrial examples summarized in Table 11 show that ore texture and mineralogical complexity remain dominant constraints regardless of the beneficiation route. Even technologically mature processes, such as magnetic separation and flotation, may exhibit unstable performance when applied to ores with variable phosphorus distribution and fine apatite dissemination.

Figure 12 shows the geographic distribution of major phosphorus-bearing magnetite ore systems and their dominant beneficiation strategies.

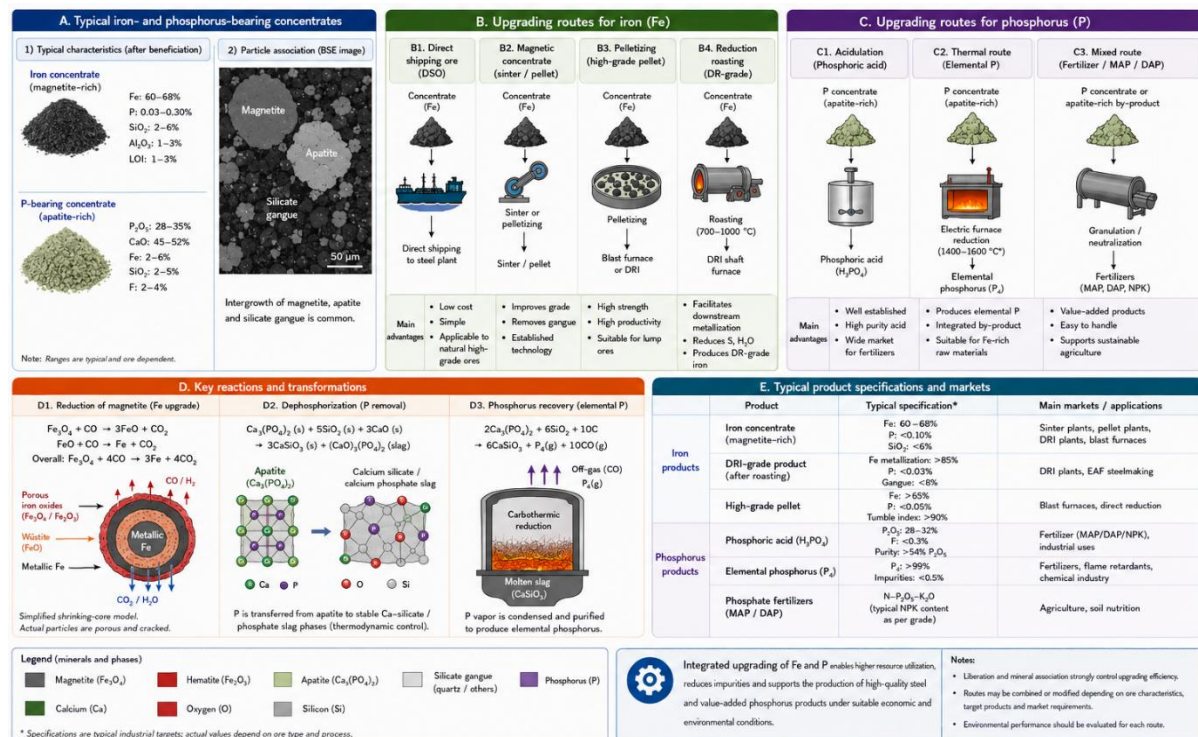


Figure 12. Geographic distribution of major phosphorus-bearing magnetite ore operations and associated beneficiation strategies. Adapted from Donskoi et al. (2022), La Cruz et al. (2020), and Tornøes et al. (2021).

Figure 12 shows that beneficiation strategies vary substantially with ore genesis, phosphorus occurrence mode, infrastructure availability, and regional industrial priorities. Chinese operations tend to emphasize thermochemical beneficiation, whereas many Western operations prioritize physical beneficiation and selective flotation. Despite these regional differences, insufficient integration between process mineralogy and beneficiation design remains a common limitation across most industrial studies.

The industrial limitations identified above reveal several unresolved scientific and technological gaps that continue to constrain the large-scale implementation of efficient dephosphorization technologies. These gaps are discussed in the next section.

## 11. Critical Gaps and Future Research Directions

Despite substantial progress in phosphorus-removal technologies for magnetite iron ores, several scientific and industrial limitations continue to hinder large-scale implementation. One of the most important gaps is the insufficient integration between mineralogical characterization and beneficiation process design. Many investigations continue to assess beneficiation performance primarily through bulk chemical analyses, while neglecting liberation behavior, intergrowth texture, and ore variability (Angelopoulos et al., 2025).

Another major limitation is the scarcity of pilot-scale and long-duration industrial investigations. Laboratory-scale experiments often use highly controlled particle-size distributions, reagent dosages, and thermal conditions that may not reflect industrial operation. Consequently, the beneficiation performance reported under laboratory conditions often overestimates the efficiency of industrial phosphorus removal (Chen et al., 2023a).

Mass balance reporting also remains inadequate in several studies. Many investigations focus primarily on phosphorus reduction while providing limited information on iron losses, gangue accumulation, water consumption, or reagent recirculation. Without comprehensive mass-balance analysis, the real industrial feasibility of the proposed routes remains difficult to assess (Apukhtina et al., 2016; He et al., 2018).

Environmental assessment is another underdeveloped aspect of the current literature. Thermochemical routes often entail elevated greenhouse gas emissions and high energy demand, whereas hydrometallurgical systems generate complex phosphorus-rich effluents that require treatment and neutralization. Nevertheless, many studies offer limited quantitative evaluation of environmental impacts or wastewater management.

Future investigations should increasingly incorporate geometallurgical approaches that integrate mineralogy, beneficiation response, ore variability, and process simulation. Automated mineralogical tools, combined with predictive modeling, may improve selection of beneficiation routes and process optimization (Baranov & Tolstov, 2026).

Machine learning and data-driven beneficiation models also represent promising research directions. Predictive models that integrate liberation behavior, mineral association, particle size distribution, and flotation response may improve process control and reduce experimental workload. However, these approaches require large, high-quality mineralogical databases, which remain relatively scarce (Ghazi et al., 2019; Gong et al., 2025).

Advanced flotation reagents and hybrid beneficiation systems also warrant further investigation. Bio-based depressants, selective hydroxamates, and environmentally compatible reagent systems may enhance flotation selectivity under complex mineralogical conditions. Similarly, integrated roasting–leaching and multiprocess systems may improve dephosphorization performance when optimized for specific ore textures (Chen et al., 2023a).

Table 12 summarizes the key scientific and industrial gaps that currently limit the development of phosphorus-removal technologies for magnetite iron ores.

Table 12. Major research gaps and future priorities for phosphorus removal from magnetitic ores. Adapted from Pereira and Papini (2015), Donskoi et al. (2022), and Xu et al. (2025).

Research gap	Current limitation	Future priority
Mineralogical integration	Limited liberation analysis	Geometallurgical modeling
Scale-up validation	Few industrial studies	Pilot-scale campaigns
Environmental assessment	Limited wastewater analysis	Integrated LCA studies
Ore variability	Static beneficiation design	Adaptive process control
Reagent selectivity	Slime sensitivity	Advanced reagent systems

The research priorities summarized in Table 12 indicate that future progress in dephosphorization technology will depend not only on improved beneficiation efficiency but also on stronger integration across mineralogy, process engineering, environmental management, and industrial scalability.

Figure 13 presents an integrated framework linking mineralogical characterization, beneficiation response, and predictive process optimization for phosphorus-bearing magnetitic ores.

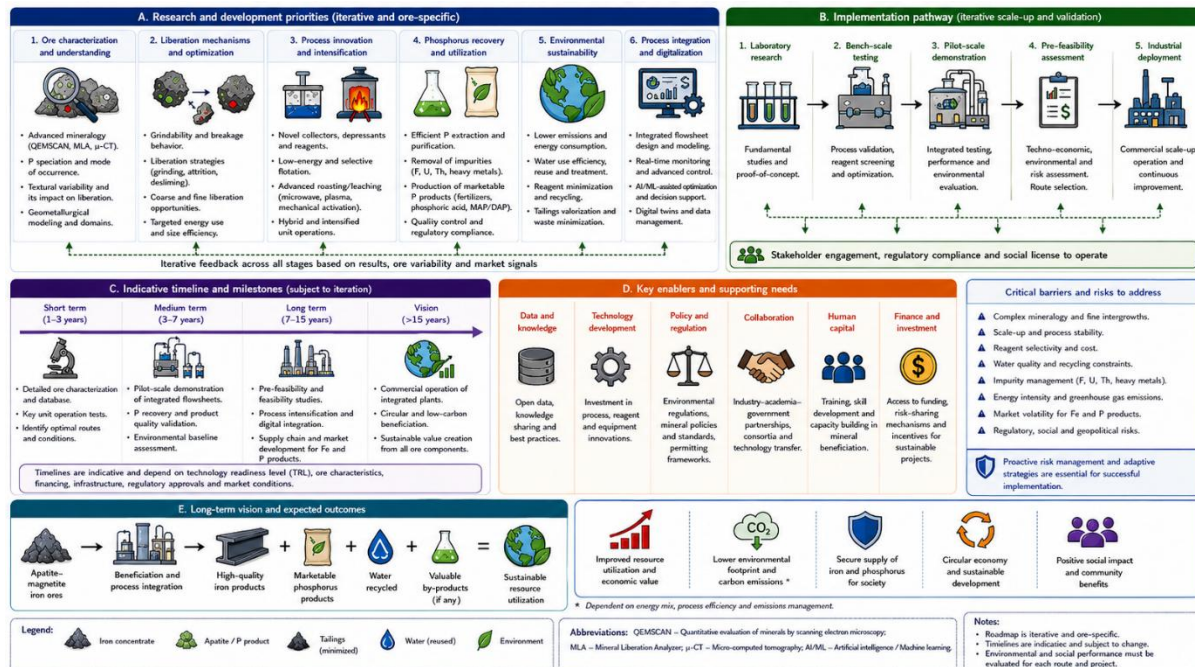


Figure 13. Proposed framework integrating mineralogy, beneficiation, and predictive process optimization. Adapted from Krolop et al. (2022), Pereira and Papini (2015), and Xu et al. (2025).

The framework illustrated in Figure 13 D emphasizes that future beneficiation strategies should move beyond isolated process optimization toward integrated geometallurgical approaches that can predict beneficiation behavior based on ore texture, liberation characteristics, and operational variability. Such integration may significantly improve industrial stability and beneficiation efficiency.

The scientific and technological challenges discussed throughout this review lead directly to the final conclusions in the next section.

## 12. Conclusions

Phosphorus remains one of the most problematic impurities in magnetite iron ores because mineralogical occurrence, liberation characteristics, and particle texture strongly control its beneficiation behavior. The review demonstrated that phosphorus does not occur exclusively as inclusions associated with magnetite but may also appear as disseminated apatite, gangue-associated phosphate minerals, fracture fillings, and fine intergrowths distributed throughout complex mineral matrices.

Physical beneficiation methods, such as magnetic separation, remain industrially attractive because of their operational simplicity and maturity. However, these processes often show limited phosphorus rejection in ores with fine apatite dissemination and composite particles. Flotation, therefore, remains the dominant strategy for selective phosphorus removal. Nevertheless, flotation performance declines substantially under conditions involving ultrafine particles, slime coating, variable water chemistry, and incomplete liberation.

Thermal and thermochemical beneficiation routes may achieve deeper dephosphorization through phase transformations and phosphorus redistribution. However, these systems remain constrained by energy consumption, operational complexity, and environmental impact. Hydrometallurgical approaches enable selective dissolution of phosphorus under controlled chemical conditions but introduce additional challenges, including reagent consumption, effluent treatment, and process economics.

Integrated beneficiation flowsheets that combine physical, chemical, and thermal operations generally deliver better phosphorus removal performance by addressing multiple mineralogical limitations simultaneously. However, integrated systems also require more advanced process control, higher CAPEX, and stronger operational integration.

One of the principal conclusions of this review is that selecting a beneficiation route should not be based solely on phosphorus concentration. Instead, process design must incorporate detailed mineralogical characterization, liberation analysis, ore variability assessment, and geometallurgical integration. Future progress in phosphorus-removal technology will therefore depend on stronger integration among process mineralogy, beneficiation engineering, predictive modeling, and industrial validation.

## **Declarations**

### **Author Contributions**

Antonio Clareti Pereira conceptualized the review, conducted literature analysis, developed the critical comparative assessment, and prepared the manuscript.

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### **Conflicts of Interest**

The author declares no conflicts of interest.

### **Data Availability**

The data supporting this review are available from the corresponding author upon reasonable request.

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