钒钛分离与提取

钒渣高效提取冶金:焙烧回转窑结圈机理与调控分析

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摘　要: 回转窑结圈是制约钒渣钠化与钙化焙烧生产连续性与钒回收率的关键瓶颈, 其本质是由内源氧化放热与外部供热叠加引发的链式反应过程。系统综述了结圈形成的微观机理、关键影响因素及工业调控策略。分析表明, 结圈并非简单的物理黏附, 而是沿“局部超温—低熔点液相生成—颗粒润湿烧结—界面黏结固化”路径动态演化的结果。其中, 钠化焙烧以低熔点钒酸钠和硅酸盐玻璃相的连续液相烧结为核心; 钙化焙烧则以高温固相致密化为基底、微量低共熔液相为辅助强化黏结。基于此, 工业上的调控策略正从经验试错转向源头干预, 主要通过控制温度场、优化原料配方及复合添加剂等手段, 精准阻断“产热-生液-黏结”的关键传递环节。为理解钒渣回转窑结圈机理及开发长效、绿色的工业调控方案提供了系统性的理论依据和实践参考。

关键词: 钒渣; 回转窑结圈; 焙烧机制; 调控策略
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听语音 聊科研 与作者互动

Efficient extraction metallurgy of vanadium slag: Mechanisms and control of ring formation in roasting rotary kiln

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Abstract: Ring formation in rotary kilns is a critical engineering issue that restricts the continuous operation and vanadium recovery efficiency of sodium and calcium roasting, with the essence of a chain reaction process caused by the combination of internal oxidation heat release and external heating. This paper reviews the formation mechanisms, main influencing factors, and control strategies of rotary kiln ring formation in sodium roasting and calcium roasting systems. Results show that ring formation is not a simple adhesion process, but a coupled evolution of local overheating, low-melting liquid-phase generation, particle sintering, liquid-phase wetting, and interparticle bonding. In sodium roasting, low melting point sodium vanadate and Na-rich silicoaluminate glass phases are the key contributors to liquid-bridge formation and particle adhesion. In calcium roasting, structural densification induced by high-temperature solid-state reactions and wetting by local low-eutectic liquid phases are the main factors sta-

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bilizing ring formation. Based on these findings, industrial regulation strategies are shifting from ordinary trial and error to source intervention. Roasting temperature control, material pretreatment, composite roasting, and multi-component additive regulation can effectively reduce the key transmission link of heat production, liquid-phase formation and bonding. This review provides a systematic theoretical basis and practical reference for understanding ring formation mechanisms and developing long-term and green industrial regulation plans industrial of rotary kiln roasting of vanadium slag.

Key words: vanadium slag; rotary kiln ring formation; roasting mechanism; sintering control

0 引言

钒是重要的战略性金属，在钢铁、化工及储能等领域应用广泛[1]。钒渣作为炼钢副产物，是工业提钒的主要原料，但其含钒物相以稳定的尖晶石固溶体形式存在，难以直接浸出[2]。因此，工业上普遍采用焙烧—浸出工艺，通过高温焙烧破坏尖晶石结构，将钒转化为可溶性盐类[3]。钠化焙烧—水浸与钙化焙烧—酸浸是当前钒渣提钒的主要工艺路线，回转窑则是实现焙烧过程的核心设备[4]。然而，在高温焙烧过程中，原料与添加剂易反应生成低熔点共熔物相，形成过量液相，显著增强颗粒间润湿与黏结能力[5]，这是导致回转窑结圈、挂壁的本质原因。结圈不仅阻碍物料运动、降低热效率，严重时还将迫使生产中断，已成为钒渣大型化连续焙烧的技术瓶颈[6]。

现有文献对钒渣焙烧的研究多集中于物相演变与提钒效率，而针对回转窑问题，相关机理与影响因素的梳理仍显零散，尤其缺乏将微观机制与宏观工艺变量相关联的系统性归纳。为此，笔者以回转窑结圈为焦点，从微观机理和宏观调控两个层面，系统综述了结圈的形成机制、影响因素与调控策略，以期为工业上长效、精准抑制结圈提供理论与实践参考。

1 回转窑的结构与运行特征

如图 1 所示，回转窑通常由倾斜布置的圆筒形窑体、耐火内衬、传动与支承装置、给料与出料系统、密封系统以及燃烧供热系统组成。与静态焙烧炉不同，回转窑不仅承担物料加热功能，还同时完成轴向输送、横向翻滚、气固换热和反应界面更新。Boateng[7] 指出，回转窑过程涉及颗粒流动、混合与偏析、燃烧、自由空间传热、料床传热及矿物加工应用等多个环节，其设计与操作直接影响物料运动状态和温度分布，进而影响结圈风险。

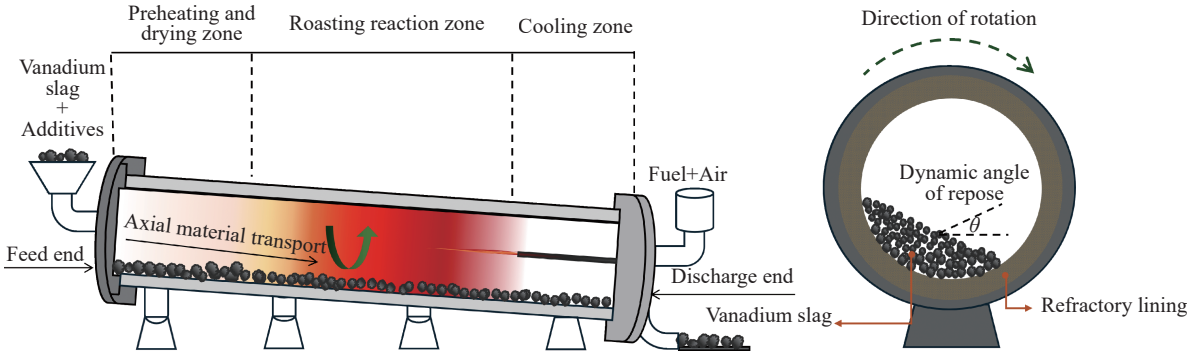


图 1 回转窑示意

Fig. 1 Schematic diagram of rotary kiln

回转窑内颗粒运动可分为横向翻滚和轴向迁移两个方面。Henein 等[8-9] 通过连续试验窑和间歇旋转筒研究了横向料床运动，指出窑速、料层深度、筒体尺寸和颗粒性质会影响物料的滑移、滚动和塌落状态；Sai 等[10] 则从停留时间分布和物料输送角度出发，发现给料量、窑体倾角、窑速、颗粒性质和挡料高度会改变物料在窑内的停留时间和输送速度。Haeldermans 等[11] 进一步在长径比为 10.5 的中试回转窑中对固体平均停留时间模型进行了验证，当窑体倾角小于 1°时，经修正的经验模型可将预测误差控制在 10% 以内。

颗粒运动决定了物料在窑内的停留时间，而供热方式则决定了温度的空间分布，二者共同影响结圈风险。从供热方式看，Gorog 等[12] 建立了火焰区传热模型，Barr 等[13] 开展了中试窑传热试验建立回转窑传热模型，指出直接燃烧式回转窑的热量主要由火焰向料层和窑壁径向传递，轴向分布并不均匀。因此，料层表面和窑衬附近容易形成较高热流

或温度梯度; 当该区域同时富集细粉或低熔点组分时, 更易发生软化、液相黏结和结圈。Tscheng[14] 在内径 0.19 m、长 2.5 m 的回转窑中, 研究了转速(最高 6 r/min)、填充率(最高 17%)、气体温度(77 ~ 317 ℃)等条件对轴向温度分布的影响。结果表明, 即使在非燃烧体系中, 气体、固体和窑壁之间也存在明显的轴向换热差异。在钒渣焙烧这类伴随强氧化放热和复杂物相反应的体系中, 窑内温度分布的不均匀性更为突出。

针对钒渣提钒工业回转窑, Wang 等[15] 在Ø3.6 m×90 m 大型回转窑中进行工业试验, 发现适宜升高并稳定控制焙烧温度有利于钒尖晶石氧化及钙钒酸盐生成, 但过高温度会诱发液相、烧结和挂壁, 最终削弱钒转化效率并导致结圈风险上升。因此, 钒渣在回转窑中的焙烧并非单一的物相转化过程, 而是设备结构、加热方式、温度分布、物料运动与自身氧化放热协同作用的结果。

2　回转窑结圈的形成

在上述设备与运行条件下, 结圈的形成可从微观演化路径和宏观影响因素两个层面加以认识。回转窑结圈并非随机发生的工程故障, 而是物料在特定温度区间内发生热化学反应的宏观表现, 本质上是烧结、黏结与挂壁行为沿温度—时间方向逐级演化的结果[16]。其演化路径如图 2 所示。从微观尺度看, 结圈起始于颗粒间的固相烧结, 粉末颗粒在热力驱动下通过界面扩散形成颈部连接, 该阶段物料虽形成一定结构强度, 但仍具有可翻动性, 尚不足以导致稳定挂壁[17]; 随着温度升高, 体系内开始生成低熔点液相, 液相以液桥形式连接颗粒, 显著降低了流动性, 使其从松散态转变为黏结态[18]。在回转窑旋转作用下, 黏结物因附着力不断在窑衬表面累积、压实, 最终固化形成具有空间分布特征的宏观结圈。因此, 结圈是颗粒在液相参与下, 其黏结行为在窑衬界面持续放大并最终空间固化的结果。

结圈主要发生于回转窑高温带, 尤其集中于物料氧化放热与外部供热叠加区域[19], 表明其形成与局部热峰值密切相关。磁铁矿及含钒尖晶石相的氧化反应释放大量热量, 可使物料局部温度远超设定值[15, 20]。在此条件下, 脉石矿物(SiO_2、Al_2O_3)与添加剂在狭窄温度窗口内迅速反应, 生成低熔点钠/钙硅铝酸盐, 引发局部而非整体熔融。这些液相以高黏度玻璃态存在, 可捕捉细小颗粒并在颗粒间铺展, 作为黏结相主导颗粒间相互作用[21], 从而导致物料黏结、挂壁, 并促使结圈层持续生长。

在局部超温与液相生成的基础上, 回转窑的运行工况进一步影响结圈的进程。窑转速过低或倾角过小会增加物料在高温带的滞留, 使黏性液相有足够时间在窑衬表面铺展、润湿, 促进颗粒捕获和结构致密化, 形成难以剥落的挂壁层[7, 22]。过高的充填率(η)则会削弱物料翻动与传热, 引发表层物料局部过热熔融, 加剧颗粒捕获行为[23]。从力学角度看, 结圈的形成与长大, 本质上是物料与窑壁间的黏附力与物料自身所受剪切应力竞争的结果, 当剥离力不足以克服黏附力时, 结圈将持续生长。

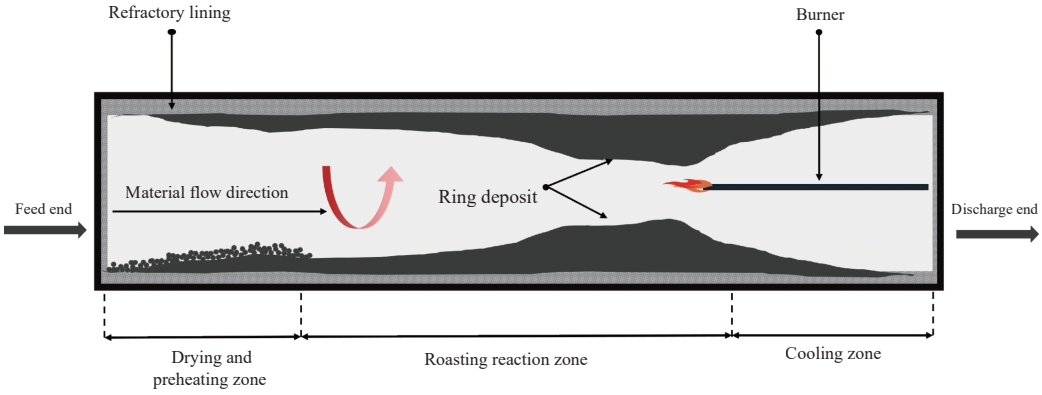


图 2　回转窑结圈机制

Fig. 2　Mechanism of ring formation in a rotary kiln

2.1　钠化焙烧工艺中回转窑结圈机理分析

钠化焙烧是当前工业提钒的主流工艺[24-25]。该工艺通过添加钠盐(如 Na_2CO_3、NaCl、或 Na_2SO_4), 将钒渣中的低价钒(如 V^{3+})氧化并转化为水溶性的钒酸钠, 钒浸出率可达到 80% 以上[26-27]。回转窑因其良好的气-固传热传质条件, 是实现该工艺的核心装备。然而, 钠盐的引入会显著降低体系中物相的熔点, 并且生成的低熔液相在回转窑动态翻滚和窑衬周期性接触作用下易发生铺展、富集和黏结, 由此引发的物料烧结和窑衬结圈已成为制约生产顺行、

增加能耗及维护成本的突出瓶颈[28]。

在焙烧初期(约 273 ~ 700 ℃),回转窑内以预热、氧化和固相反应为主[20]。当温度进一步升高至 650 ~ 900 ℃,物料进入氧化带与烧成带,钒被逐步氧化至高价态,并与 Na_2O 反应生成偏钒酸钠($NaVO_3$)、焦钒酸钠($Na_4V_2O_7$)、正钒酸钠(Na_3VO_4)等可溶性的钒酸钠盐[29-30],其熔点分别为 630、658 ℃ 和 866 ℃。其中,$NaVO_3$、$Na_4V_2O_7$ 熔点较低,是体系中最早出现的低熔点液相,在实际焙烧温度条件下极易发生软化或局部熔融[29-32]。

焙烧过程中 Na_2O 还会与 SiO_2、Al_2O_3 等脉石组分发生反应。铁橄榄石等物相分解后,可与钠盐生成硅酸钠(Na_2SiO_3)、锥辉石($NaFeSi_2O_6$)、钠长石($NaAlSi_3O_8$)等复合硅酸盐[33-35],其主要反应如式(1)~(3)所示。这些物相在高温下会进一步转变为富钠的低熔点硅酸盐玻璃相,其软化温度低于原始硅酸盐矿物(如铁橄榄石,熔点约 1 205 ℃),并呈高黏度、非晶态特征[36-37]。

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow \quad (1)$$

$$Fe_2SiO_4 + 3SiO_2 + Na_2CO_3 + 1/2O_2 \rightarrow 2NaFeSi_2O_6 + CO_2\uparrow \quad (2)$$

$$Al_2O_3 + 6SiO_2 + Na_2CO_3 \rightarrow 2NaAlSi_3O_8 + CO_2\uparrow \quad (3)$$

从微观本质上看,Na^+作为网络修饰体参与硅酸盐结构调控,通过打断 Si–O–Si 桥氧键降低了体系聚合度,使其熔点显著降低并在更低温度下形成液相[38]。随着温度进一步升高,液相量增加的同时,其内部硅氧结构发生重排,形成高黏度熔体,展现出极强的润湿性和黏结能力[39]。硅酸盐熔体结构研究[40]表明,碱金属和碱土金属阳离子可通过改变 Q*n* 结构单元分布和网络聚合程度影响熔体黏度、构型熵和流变行为,因此 Na^+富集不仅降低液相形成的温度,也会改变液相对颗粒和窑衬的润湿黏结能力。该类高黏度玻璃相虽不直接决定钒的转化效率,却在空间尺度上显著放大了颗粒黏结行为,是结圈能够稳定生长、难以剥落的关键原因。钠化焙烧结圈机理如图 3 所示。

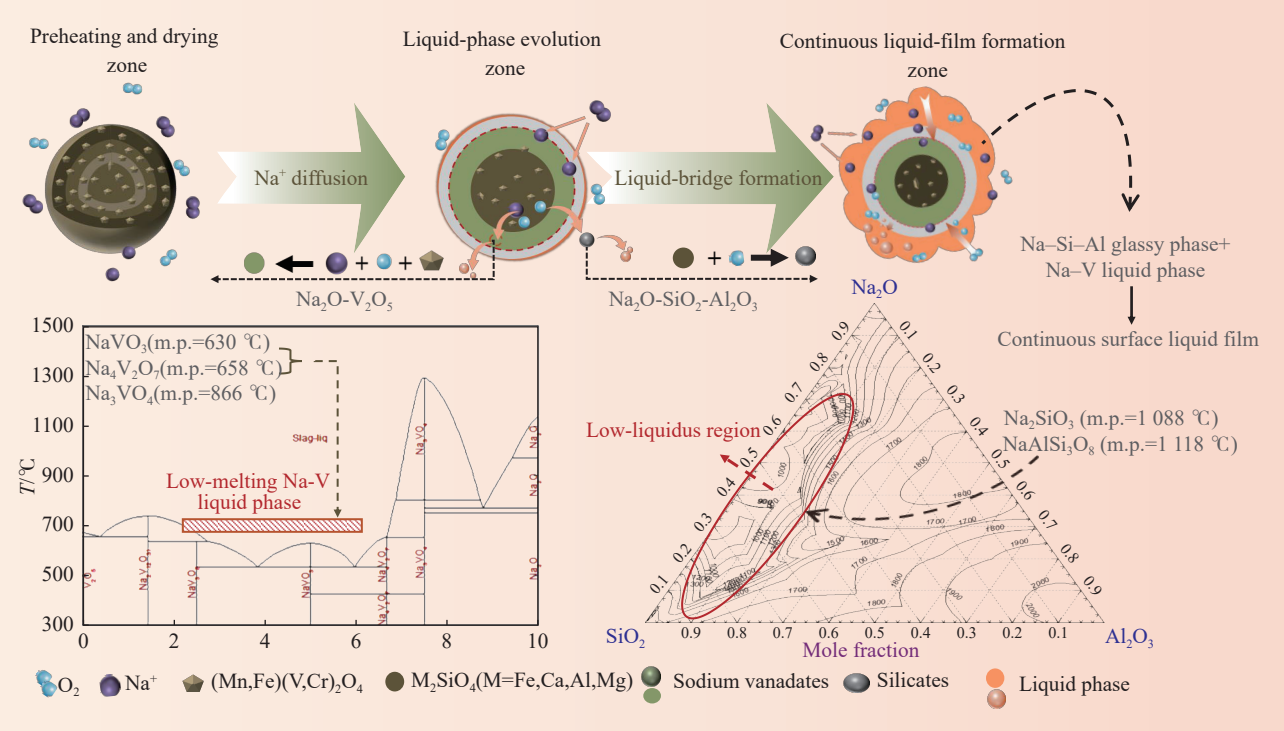


图 3 钠化焙烧结圈机理

Fig. 3 Mechanism of ring formation in sodium-roasting process

在含铬等复杂钒渣体系中,Na^+的消耗路径不仅受钒酸盐生成控制,还受到铬尖晶石氧化矿化反应的影响。高铬钒渣中 Cr 多以 $(Mn,Fe,Mg)(V,Cr)_2O_4$ 等尖晶石形式存在,在钠化焙烧过程中,Cr^{3+}可被氧化并与 Na_2CO_3 反应生成水溶性 Na_2CrO_4[29, 41]。赵卫夺等[42]研究发现,仅以 Na_2CO_3 为焙烧助剂时,钒和铬会发生同步浸出,说明 Na^+不仅参与钒酸钠生成,也会大量进入铬酸盐相;当引入 CaO 后,Ca^{2+}可优先与硅铝杂质结合生成高熔点硅酸钙,释放部分游离 Na^+,进一步促进铬尖晶石向 Na_2CrO_4 转化。

因此, 含铬体系中的 Na^+分配并非单一指向钒酸盐, 而是在钒酸盐、铬酸盐和钠硅酸盐之间发生竞争。若 Na_2CO_3 用量不足, 部分铬尖晶石难以充分氧化; 若 Na_2CO_3 过量, 则易生成低熔钠硅酸盐和钠系共熔物, 包裹未反应尖晶石并加剧烧结[43-44]。由此可见, 铬的存在不仅增加了钒铬分离难度, 也会通过改变 Na^+分配和液相组成, 增强低熔液相的连通性, 从微观层面放大钠化焙烧结圈趋势。

工业实践表明, 钠化焙烧结圈主要发生在回转窑高温区段, 特别是物料氧化放热与外部供热叠加的区域。相关研究[19, 45] 证实, 磁铁矿及含钒尖晶石相的氧化反应会释放大量反应热, 可使物料局部温度高于设定焙烧温度(800 ~ 1 000 ℃), 形成局部超温。这种由内源反应放热与外源供热协同引发的超温现象, 是触发低熔点液相生成、物料软化并最终导致黏附结圈的能量基础。

2.2　钙化焙烧工艺中回转窑结圈机理分析

钙化焙烧是一种环境友好的清洁提钒工艺, 通过添加钙基添加剂(石灰或石灰石)将钒转化为酸溶性钒酸钙[46]。然而, 其工业回转窑同样面临严重的结圈问题。研究表明, CaO、FeO 及 SiO_2 等组分反应生成的低共熔物会引发物料局部熔融和炉衬黏附[18, 47-48]。在极端工况下, 可形成直径超 1 m 的高强烧结球, 结圈层厚度可达 58 cm, 导致回转窑有效内径从 3.1 m 锐减至 1.7 m, 严重恶化传热与物料运动, 迫使频繁停窑。与钠化焙烧的低熔点液相主导机制不同, 钙化焙烧结圈的核心驱动力是“固相为主, 液相为辅”, 由局部超温、高温固相反应致密化以及脉石-杂质引发的多元低共熔行为三者共同驱动。钙化焙烧结圈机理如图 4 所示。

从空间分布特征看, 钙化焙烧结圈具有明显的区域选择性, 集中于回转窑高温反应区及恒温段, 特别是在物料完成主要氧化反应并进入稳定高温段后, 结圈倾向更加明显[18]。在该区域内, FeV_2O_4、Fe_3O_4 等尖晶石矿物的剧烈氧化放热与回转窑外部供热叠加, 可使局部温升超过 200 ℃, 料层表面及颗粒接触密集处更容易出现局部过热, 在名义焙烧温度 850 ~ 900 ℃ 的条件下形成超 1 000 ℃ 的局部超温区[48-49]。这种热量叠加效应致使高熔点钙钒酸盐及脉石相发生结构重排与局部共熔, 并显著加速其致密化进程, 为结圈提供初始的热力学与动力学条件。由于尖晶石相多被硅酸盐和辉石相包裹, 钙化焙烧反应初期受扩散过程限制, 过程相对缓慢[50-51]。在 640 ~ 800 ℃, 脉石中橄榄石相分解产生的 SiO_2 可与 CaO 反应生成高熔点 $CaSiO_3$(熔点约 1 540 ℃)并保持固态[52], 这使得钙化焙烧早期难以形成连续液相, 奠定了以固相反应为主的烧结基础。

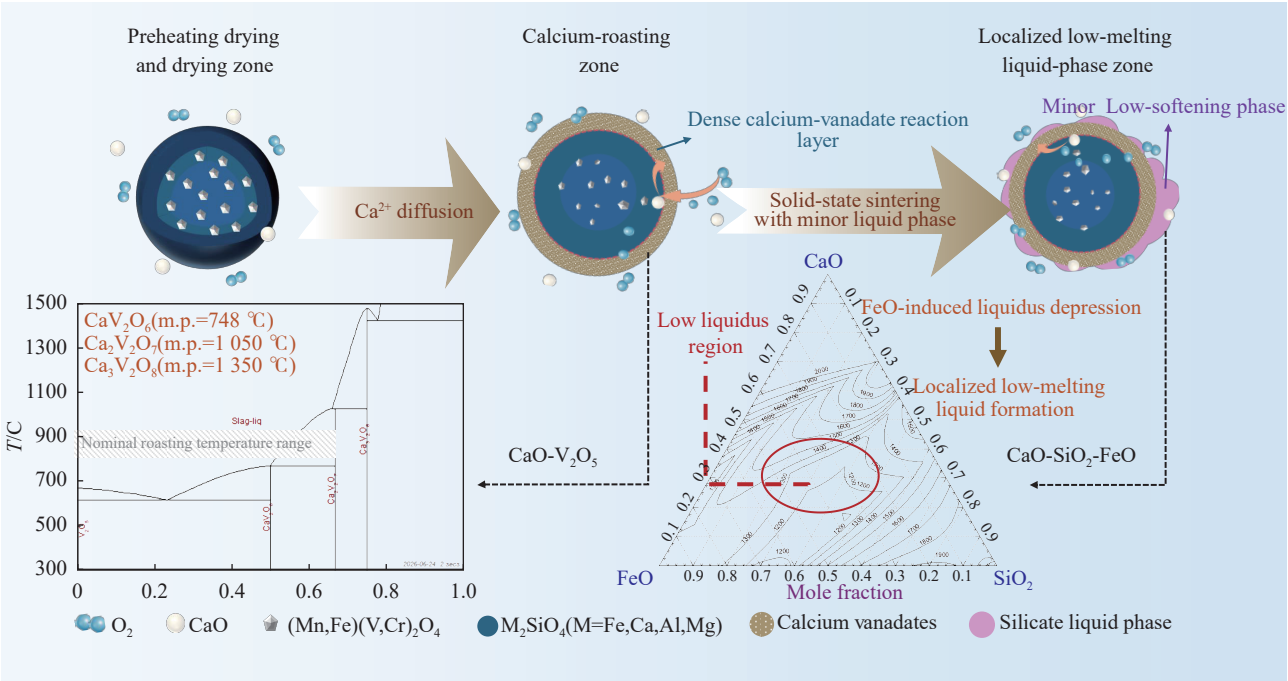


图 4　钙化焙烧结圈机理

Fig. 4　Mechanism of ring formation in calcification-roasting process

与此同时, 尖晶石相在 500 ~ 850 ℃ 逐步氧化, 钒由尖晶石结构中释放并与 CaO 反应生成偏钒酸钙(CaV_2O_6)、焦钒酸钙($Ca_2V_2O_7$)、正钒酸钙($Ca_3V_2O_8$)等钙钒酸盐物相[53-54]。该反应由表面反

应控制逐步转向扩散控制，生成的钒酸钙盐在颗粒表面形成一层致密的反应壳层，阻碍了 Ca^{2+}、O_2 等的进一步传质，但促进了颗粒间的紧密贴合与固相烧结[55]。这一烧结体即成为后期结圈的初始核心。此外，反应过程中生成的钒青铜（$Ca_{0.33}V_2O_5$）等中间相，因其结构稳定性，能进一步加强反应层的致密性，使得这一初始核心更为稳固[56]。过高的焙烧温度是诱发钙化焙烧烧结和结圈的首要因素。当温度超过约 850 ~ 900 ℃ 时，物料发生显著致密化，孔隙率急剧下降，气体扩散受阻[57-61]。

在固相致密化的基础上，组分偏析会诱发局部液相的生成。当 CaO 过量且脉石中 SiO_2、Al_2O_3 含量偏高时，会生成 $CaO–SiO_2–Al_2O_3$ 基低熔硅铝酸盐[62-64]；在含铁氧化物等杂组分的多元实际渣系（$CaO–SiO_2–Al_2O_3–FeO_x$）中，FeO_x 可降低硅灰石/黄长石初晶区的液相线温度，使该类低熔物的初始液相温度降至约 1 000 ~ 1 100 ℃，这与回转窑高温区局部超温的条件高度重合，因而成为局部液相的重要来源[65]。因此，精钒渣中磁性物含量偏高时，不仅会增强高温氧化放热和局部热峰值，还会提高 FeO_x 参与低熔硅铝酸盐液相生成的可能性，从而加剧钙化焙烧过程中的烧结和结圈风险。Zhao 等[66] 指出，该过程与钠化焙烧中钠盐作用机制具有相似性，均通过 Ca^{2+} 或 Na^+ 破坏硅氧网络结构，把原本高度聚合的网络结构进行解聚，从而降低了熔点。Xuan 和 Isaksson 等[67-68] 也发现，当体系中 SiO_2、Al_2O_3 等网络形成体含量较高时，解聚生成的 $[SiO_4]/[AlO_4]$ 基元在高温下会重新缩聚成复杂阴离子团簇，导致液相黏度显著升高。因此，在高温预致密化的物料中，这种高黏度硅铝酸盐熔体会在颗粒间形成强力黏结，将已致密的块体进一步连接固定，最终形成结构坚固、难以清除的结圈层。

此外，微量杂质元素（如 Cr、Al、Mn、Ti）对结圈过程也存在显著影响[59, 69-71]。这些元素在高温下进入晶格会引起局部畸变。较小离子（Cr^{3+}、Al^{3+}）导致晶格收缩，较大离子（Mn^{2+}、Ti^{4+}）则引起膨胀。这种局部晶格畸变，一方面增强了颗粒自身的反应活性，另一方面促进了低熔点液相的生成与固相烧结。这种影响会从局部逐步扩展至整体，持续加剧烧结程度，构成稳固结圈形成的微观内在驱动力。

3 回转窑结圈主要调控策略

3.1 钠化工艺回转窑结圈调控策略

基于上文对结圈机理的分析，热工条件、机械参数和氧化状态等是调控结圈的关键外部因素。鉴于金属铁在高温区的剧烈氧化放热是导致局部过热的主因之一，工业生产中需严格控制钒渣中的金属铁含量。在链篦机—回转窑焙烧钒钛磁铁矿的工艺中，通过强化链篦机阶段预氧化使球团 FeO 含量降低至 0.37% 以下，此时磁性物含量降低，氧化放热峰值与高温焙烧区间不再发生叠加，可有效减少 1 225 ~ 1 300 ℃ 区间高温液相生成，从而显著缓解回转窑内烧结与结圈问题[19]。

在此基础上，降低焙烧温度是抑制液相生成最直接的思路。尽管高温有利于钒酸盐转化，但液相量的急剧增加会严重恶化回转窑操作。为平衡这一矛盾，工业上常采取“低温焙烧-返料焙烧”的策略。将焙烧温度适当降至 800 ℃ 以下，虽会导致钒一次转化率偏低、尾渣残钒升高，但通过将浸出尾渣返回配料系统进行二次焙烧，可有效弥补这一缺陷。该策略具有多重优势：其一，浸出尾渣已基本氧化完全，可显著减少窑内反应热的过量释放；其二，尾渣作为惰性稀释剂，可降低高温液相的比例；其三，二次焙烧能进一步促进残存钒的转化，提高总收率。该策略与铬精矿钠化焙烧中为降低液相比例而浸出尾渣返料焙烧的操作原理相似，但会导致生产效率降低，不利于提高产能。基于钠化焙烧结圈以低熔钠钒酸盐和富钠硅酸盐液相黏结为主的特征，抑制结圈的关键在于削弱氧化放热峰值、避开液相快速生成温区，并通过运行参数和添加剂阻断液相在颗粒—窑衬界面的连续铺展。为比较不同措施对钒转化效率、焙烧温度、添加剂用量及低熔相生成行为的影响，钠化焙烧典型调控策略如表 1 所示。Deng 等[31, 36] 提出通过电场强化和过硫酸盐协同的低温钠化焙烧技术，在约 650 ℃ 即可完成钒转化，从热力学上规避了 SiO_2 大量溶入液相的温度区间，可有效抑制烧结与玻璃相包裹。

通过添加剂进行原料组成的微观调控，是实现结圈源头抑制的另一关键路径。Li 等[72] 发现 K^+ 能有效拆解硅酸盐网络，具有抑制物料黏结的潜力。Yang 和张成强等[73-74] 提出钾钠复合焙烧，利用 Na^+/K^+ “混合碱效应”，在 750 ~ 800 ℃ 条件下促进钒的协同活化，同时调节硅氧网络结构，改善高温液相流变行为，拓宽了工艺窗口。针对高硅体系中钠硅酸盐液相过量的问题，Bai 等[75] 引入 CaO，可与 SiO_2 反应生成高熔点硅酸钙（如 Ca_2SiO_4），减少低熔点硅酸钠的生成，降低结圈倾向。曹帅等通过在钠化体系中适量引入 MgO，与 Na+协同生成高溶解度钠镁复合钒酸盐（$Na_6Mg_2V_4O_{15}$），在避免难溶镁钒酸盐生成的同时提高了水浸条件下钒的迁移能力，实现了

降钠与提效的协同优化。Tang 和 Liu 等[77-78] 则引入 MnO_2 作为促氧化添加剂, 利用 Mn^{4+}/Mn^{3+}循环加速低价钒的氧化过程, 使反应可在 700 ℃ 左右进行, 也可规避高温过熔的风险。Li 等[79] 提出氧化铈(CeO_2)催化钠化焙烧方法, 利用 CeO_2 产生的氧空位激活 Ce^{3+}/Ce^{4+}氧化还原循环, 提高氧利用率, 加速钒的氧化, 促进稳定可溶钒酸盐($Na_4V_2O_7$)的生成。此外部分工业专利[80-83] 已从回转窑结构供氧、富氧分段焙烧和尾渣返配等方面给出了较为直接的工程化指标, 包括无结圈运行时间、钒转化率提升幅度、焙烧产物形貌及异常工况下结圈出现时间等, 可为钠化焙烧防圈效果评价提供补充依据。

关于回转窑颗粒输运的研究表明[84-87], 窑体倾角、转速、填充率、给料量和挡料结构会影响物料滞留、料层深度和轴向输送行为。对于钠化体系, Kerby 等[32] 的相平衡研究和秦明晓等[88] 的钠化焙烧研究表明, 含钠钒酸盐体系具有较低温度下形成液相的可能, Na_2CO_3 可促进钒铁尖晶石分解并生成 $NaVO_3$ 等含钠钒酸盐物相。因此, 当 $NaVO_3$、$Na_4V_2O_7$ 及富钠硅酸盐液相在高温区生成后, 过长停留时间会增加其铺展、黏附和固化风险; 而停留时间过短又可能导致低价钒氧化和钠化成盐不足。

表 1　钠化焙烧典型调控策略效果对比

Table 1　Comparison of typical control strategies for sodium-roasting

Strategy	Key conditions			Performance and ring-control effect	
	Temperature/℃	Composition/%	Other conditions	V Rate/%	Ring-control effect
Low-temperature roasting[31,36]	≤650		Electric field or oxidant; field + persulfate	Leaching: 87.74; 95.64	Less low-melting liquid
Pre-oxidation-assisted roasting[19]		FeO <0.37		Conversion: 85.6	Less FeO–SiO_2–Na_2O eutectic adhesion
K–Na co-roasting[72-74]	750 ~ 900		K_2SO_4; n(Na)/n(K) ≈ 1	Leaching: 41.17 → 71.37	Lower melt viscosity
Na–Ca co-roasting[75]			Na_2CO_3–$CaCO_3$; CaO binds SiO_2	Leaching: 71.9 → 75.19	Less glass-film formation
Na–Mg co-roasting[76]		MgO 3; Na_2CO_3: 20 → 18		Leaching: 85.30 → 90.38	Less Na-silicate formation
Catalytic oxidation[77-79]			MnO_2 or CeO_2	Leaching: 94	Enables lower-temperature roasting
Internal O_2 supply[80]	T_{max}: 730	O_2: 22	O_2 pipe	Conversion: 83.3 → 96.2	Ring-free for 62 day
O_2-enriched staged roasting[81]		O_2: 10 ~ 25	Staged control	Conversion: 90 ~ 96	Improves gas–solid transfer
Two-stage sodium roasting[82]	650 ~ 760; 740 ~ 820			Conversion: 90.75 ~ 93.30	Avoids local overheating
Tailings recycle + aerobic roasting[83]	800 ~ 900	O_2 ⩾10		Conversion: 84.26 ~ 86.84	Dilutes liquid phase

3.2　钙化工艺回转窑结圈调控策略

钙化工艺回转窑结圈典型调控策略如表 2 所示。控制钙化焙烧温度上限是避免低熔点相熔融的最直接措施, 但为了保证一定的钒转化率, 焙烧温度仍需高于 850 ℃[47-48], 若结圈明显或钒一次转化率低, 仍需要浸出渣返料进行二次焙烧。石灰添加量不宜过高, 钙钒比控制在 $n(CaO)/n(V_2O_5) = 0.5 \sim 1.0$, 以抑制低熔点硅酸盐的过量生成[58, 60, 89-90]。现场生产实践表明, 通过风选机严格控制精钒渣磁性物含量低于 3%, 并稳定在 2% 以内, 可明显改善同等工况下的窑况稳定性, 降低结圈倾向。对物料进行预处理, 如采用高能球磨, 可显著增加钒渣比表面积并引发晶格畸变, 使最高反应温度降低约 100 ℃, 从而远离烧结温区, 避免高温下直接烧结与窑衬黏附[91-92]。在工业实践中, 也采用“预钙化钒渣循环焙烧”策略, 可优化窑内放热曲线, 稳定窑温(≤1 153 K), 从而成功抑制结圈[48]。微波焙烧则因其体积加热和热应力大的特点, 能够在物料中产生更多裂纹与孔隙, 形成疏松结构, 在一定程度上缓解了致密化烧结倾向[93-95]。

除温度制度、碱度和物料预处理外, 钙化焙烧还应关注回转窑运行过程的动态稳定性。张菊花等[96] 研究发现升温速率、保温温度和保温时间会影响钒渣钙化氧化效率; Wang 等[15] 在大型回转窑工业试验中指出, 给料量、窑速、温度稳定性、负压和燃烧配比的合理匹配是获得稳定钒转化率的重要条件; 攀钢相关专利[97] 也强调, 参数波动易造成焙烧产物夹生或结圈, 而稳定温度、负压和气体流量有利于获得疏松、易破碎的焙烧产物。除实验室研究中常用的钒浸出率、焙烧温度和产物结构等指标外, 工业专利[80, 97-99] 也给出了连续运行时间、温度波动范围、焙烧产物形貌及钒转化率等工程化结果, 可作为评价钙化焙烧回转窑防圈措施工业适用性的补充依据。

通过复合焙烧与多组分添加剂调节渣相物相组成和液相流变特性, 可从微观层面实现对结圈的抑制。其核心在于引入第二种阳离子(如 Mn^{2+}、Mg^{2+}、

Ba^{2+}、Ce^{3+}/Ce^{4+}），与 Ca^{2+}产生协同效应，促进钒的高效转化，减少高温区的停留时间，间接减轻物料烧结，如 $BaCO_3/CaO$[100]、CeO_2/CaO[101]、MnO_2/CaO[102]、MgO/CaO[103-104,105] 复合焙烧技术。

表 2 钙化焙烧典型调控策略效果对比

Table 2 Comparison of typical control strategies for calcification-roasting

Strategy	Key conditions			Performance and ring-control effect	
	Temperature / ℃	Composition/%	Other conditions	V Rate/%	Ring-control effect
Alkalinity optimization[50]			$n(CaO)/n(V_2O_5)$ = 0.5 ~ 1.0		Excess CaO increases low-softening phases
Magnetic material separation		Magnetic material <3			Less oxidation heat and FeO_x-related liquid
Mechanical activation[91-92]	≈800		High-energy milling		Enhances low-temperature reaction; less sintering
Pre-calcification recycling[48]	⩽880		Recycle pre-calcified material		Stabilizes heat release; suppresses rings
Microwave calcification roasting[94]			Microwave + $Ca(OH)_2$		Creates cracks/pores; less densification
$CaO–BaCO_3$ composite[100]			Ba/Ca additive		Industrial ring-control validation needed
CeO_2 catalytic roasting[101]			Ce^{3+}/Ce^{4+} redox cycle	Leaching: up to 93.17	
$CaO–MnO_2$ composite[102]			Mn redox cycle	Leaching: up to 91.62	Lower overheating risk
CaO–MgO composite[103-104]	850		n(CaO)/n(MgO) ≈1:1	Leaching: 91.20	Suppresses continuous liquid films
Internal O_2 supply[80]	850	O_2 :19	O_2 pipe	Conversion: 81.2 → 94.8	Ring-free for 50 day
O_2 -enriched calcification[98]	830 ~ 880	O_2 :12 ~ 21		Leaching: 88.42–89.82	Avoids sintering zone
Two-stage calcification[99]	800 ~ 850; 840 ~ 900			Conversion: 91.16–92.97	No rings in industrial test
Stable parameter control[97]			Feed, speed, temperature, pressure and gas control	Conversion: 85–92	Loose products; fewer rings

4 结论与展望

4.1 结论

1）回转窑结圈是局部超温、液相生成与固相致密化协同作用的结果。钒渣中金属铁、磁铁矿及含钒尖晶石的氧化放热与外部供热叠加，在高温区形成局部超温，诱发低熔点液相生成和固相烧结；物料在窑内反复翻滚、压实并与窑衬接触，逐渐由松散颗粒转变为黏结沉积层，最终形成稳定结圈。局部超温是结圈发生的重要诱因，液相黏结与固相致密化决定了结圈的持续生长。

2）钠化焙烧结圈主要受低熔点钠系液相控制。$NaVO_3$、$Na_4V_2O_7$ 等钒酸钠在较低温度下即可发生软化或熔融，Na_2O 与 SiO_2、Al_2O_3 反应生成的富钠硅酸盐玻璃相进一步增强了液相的润湿与黏结能力。因此，钠化焙烧防结圈的重点是控制局部热峰值和高温停留时间，减少低熔点钠系液相的生成及连续化分布。

3）钙化焙烧结圈以高温固相反应引起的颗粒致密化为主，局部低软化液相起强化作用。钒酸钙等反应产物在颗粒表面形成致密反应层，高温下颗粒孔隙减少并逐渐烧结；当 CaO、SiO_2、Al_2O_3 和 FeO_x 等组分发生局部富集并与超温区重合时，生成的少量低熔点硅铝酸盐液相进一步增强黏结。因此，控制焙烧温度、CaO 配比、磁性物含量及高温区料层状态是减轻钙化焙烧结圈的关键。

4.2 展望

1）机理层面，应结合高温原位表征、热力学计算和多尺度模拟，揭示液相生成、颗粒黏附、固相致密化和窑衬固定的动态演化规律。

2）过程监测层面，应融合工业大数据、CFD–DEM 模拟，构建结圈风险实时识别与预警模型，推动回转窑运行由被动清圈向主动防圈转变。

3）绿色调控层面，应加快低温焙烧、微波焙烧和电场辅助等新工艺的连续生产验证，并基于 CALPHAD 计算优化复合添加剂，在减轻结圈的同时兼顾提钒效率与工业运行稳定性。

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