Supplementary data for

Whole-Process Pollution Control for Cost-Effective and Cleaner Chemical Production—A Case Study of the Tungsten Industry in China

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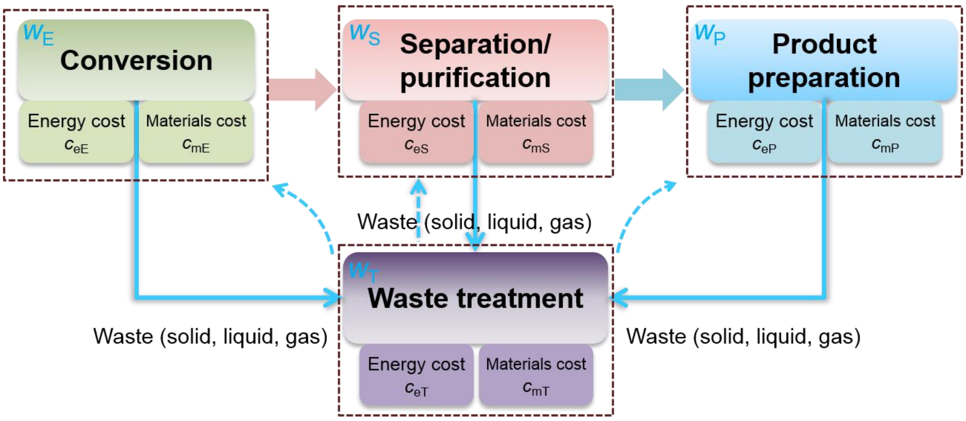
GRAPHIC ABSTRACT



Whole Process pollution control: Combination of cleaner production and waste treatment

Table S1

Life cycle impact assessment values for tungsten mineral processing (from mineral to products)

Categories	Value	GSD^2
Carcinogens	3.00×10^{-4} CTUh	1.81
Climate change	6.85×10^4 kg CO_2 eq	1.44
Fossil depletion	1.57×10^4 kg oil eq	1.32
Freshwater ecotoxicity	2.82×10^5 CTUe	2.26
Photochemical oxidant formation	178.63 kg NMVOC	1.44
Particulate matter formation	80.46 kg PM_{10} eq	1.34
Terrestrial acidification	212.62 kg SO_2 eq	1.32
Marine eutrophication	13.96 kg N eq	1.29
Non-carcinogens	5.05×10^{-3} CTUh	1.80
Ozone depletion	4.81×10^{-4} kg CFC-11 eq	2.12
Agricultural land occupation	284.89 m^2a	2.03
Urban land occupation	321.37 m^2a	1.67
Water depletion	597.01 m^3	1.28
Metal depletion	501.54 kg Fe eq	1.61
Freshwater eutrophication	0.28 kg P eq	1.58

GSD^2: the squared geometric standard deviation.

Taking tungsten as a representative metal, life cycle analysis is possible to identify the environmental impacts [8]. The values of the aspects for a specific tungsten-bearing product are given in Table S1 [11]. It can be noticed that carcinogens and water ecotoxicity are two factors of the most significant contributions to the environmental impacts. Criticality analysis of W has been carried out considering the supply risk and economic importance [2,7], in which substitutability and susceptibility of the considered metal are both included. However, both life cycle analysis and criticality analysis provide corresponding information in view of the global/regional environment and economy conditions. When a process/plant requires process optimization in accordance to specific cost analysis or new environmental regulations, both methodologies are not fully suitable and their databases may not be applicable for this specific circumstance. The environmental impacts in plant-scale for lateral comparison among different processes of a specific product are also rarely reported [12]. To ensure the sustainability of the metal supply and to understand both the economic and environmental implementation of their production, it is important to systematically analyze the on-site production process, especially in terms of the production cost and the potential to reduce costs and environmental impacts (i.e., pollution). In China, P1 was the dominant process during the period of World War II and before the 1970s. Most of the tungsten produced via APT production during that period was exported to Russia, the USA and European countries. Currently, China still accounts for more than 80% of the primary tungsten market.

Concerning process optimization, two types of approaches are usually applied: 1) new technology is implemented to improve the reaction or material conversion efficiency and 2) effective pollutant treatment technology is implemented for valorization of the pollutants into potential products or for detoxification. In both cases, the landfilling of waste can be reduced, and the effectiveness of material conversion can be improved, both of which are in line with the objectives of cleaner production and a circular economy [16,17]. Meanwhile, process cost or comprehensive cost of a plant is a critical factor being a driving force for implementation of such optimization. It is possible to incorporate concepts related to environmental management, including life cycle assessment (LCA) and sustainable management during process optimization to ensure the effectiveness of optimization and fulfill the environment quality requirements of relevant policies [18,19]. When evaluating the effective environmental management and economic competitiveness of the rare/critical metals supply, it is important to understand the significance of a process optimization technology and to quantitatively evaluate the importance of cleaner production and waste/emission treatment.

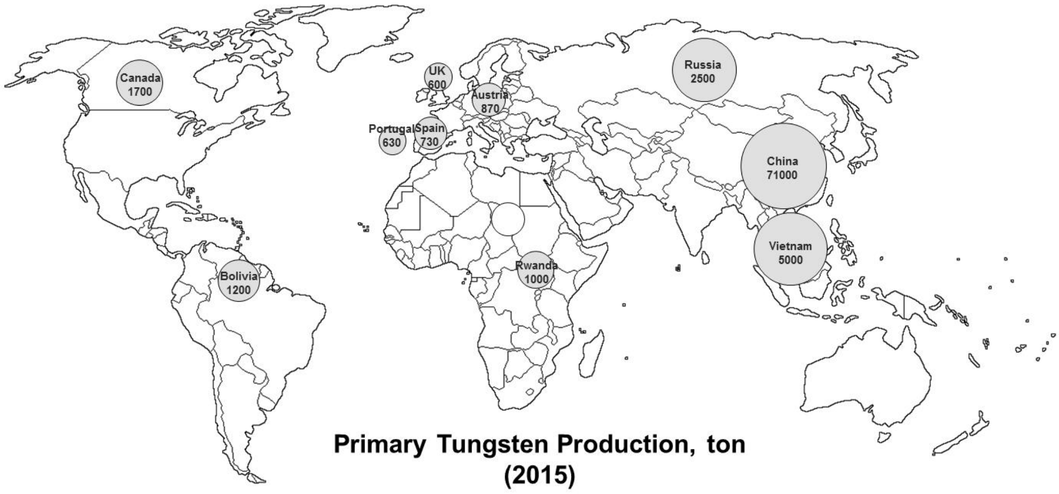
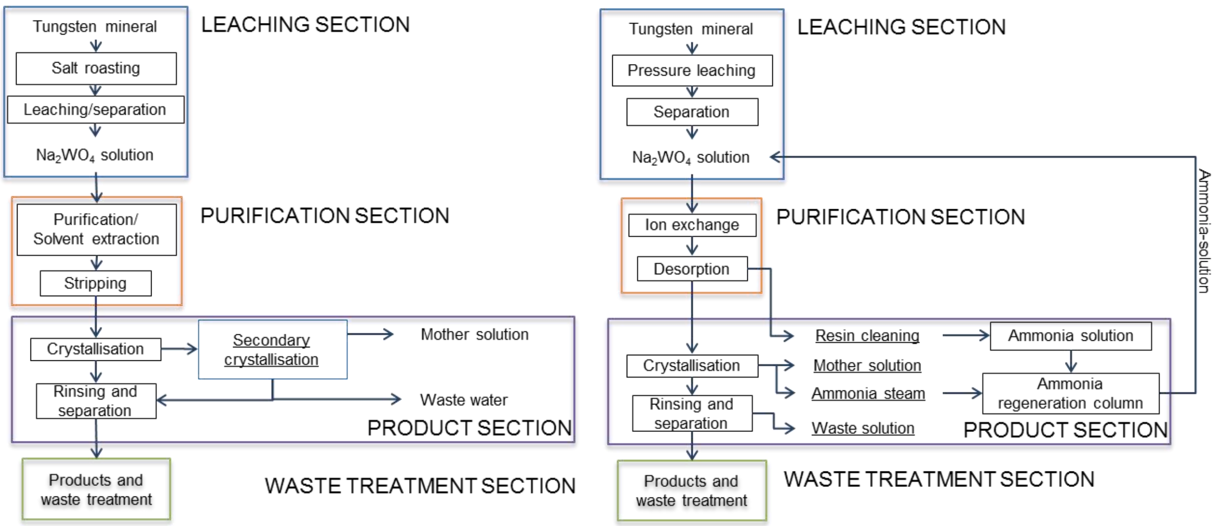


Fig. S1. Global primary tungsten production rate in 2015 (estimated)

So far, there is still no well-established methodology to evaluate the effectiveness of a process optimization to simultaneously understand both the pollution control level and process profit. Life cycle analysis in accordance to the principles of cleaner production can be used to evaluate the environmental impacts/burdens including global warming potential, ecosystem damage, and human health implications and so on [8]. However, process cost or profit is not involved. In terms of the ISO 14000 standard analysis procedures, it is possible to indirectly implement costs related to environmental impact and energy consumption while the process cost related to resource efficiencies and waste/emission treatment is not directly considered in such assessment [9]. For the economic aspect of a process for metal production, a term of economic importance (EI) is defined in materials criticality analysis to discuss the importance of a material associated with industrial megasectors in a specified region and their gross value added (GVA) [10]. However, it is still not possible to properly evaluate the process cost in order to provide guidelines or implement the factor of process profit during process optimization. As a new technology, the ion exchange process was introduced to improve the tungsten extraction selectivity at the end of the 1970s, although in China both P1 and P2 continue to be used.



(a) (b)

Fig. S2. A typical process for APT production (a) salt roasting process and (b) process considering WPPC

During extraction, caustic soda is used to roast with scheelite concentrate at around 1073 K. Subsequently, the roasted material is leached with water or sodium carbonate to obtain a leaching solution with tungsten and a residue mainly with calcium oxides and minor amount of heavy metals. The sodium paratungstate solution is further purified and extracted to obtain a solution with APT which is ready for APT production. The residue and waste water are usually delivered to certified companies/locations for treatment/landfilling. Waste gas is usually treated with the facilities already in the plant. In this roasting-leaching process, about 89% tungsten can be claimed by roasting the concentrate at 1073 K for 4h under the oxidizing conditions.

As previously mentioned, the optimization of an industrial process for the production of critical materials is in practice usually based on the technological/facility improvement of a single step or a small section of the whole process. The implementation of new technology throughout the whole process or in a significant portion of the process is usually difficult to adopt in practice because of the risk of large profit loss. However, the drawbacks of improving a single step include 1) the difficulty associated with precisely evaluating its effect on the material effectiveness and environmental impact of the whole process after the improvement, which usually requires additional investment, and 2) the significant number of operations needed to determine its influence on the production cost, even if the efficiency improvement is clear. Consequently, practical innovation in this field in industry is slow, and the progress towards cleaner production of metal materials is fairly slow [25]. To address this issue, a whole process pollution control (WPPC) methodology is proposed together with a case study and technological innovation for the production of APT in the Jiangxi area of China.

Additionally, pH is an important factor to control in this step, and assisting reagents (e.g., PAM) must sometimes be added. Organic solvents, including primene JM-T, primary amine N1923, TOA and DIDA, are frequently used for solvent extraction of W from halide leach solutions [30,31]. The leaching solution needs to be adjusted to a pH range of 2~4 before tungsten can be extracted selectively into the organic phase. The tungsten-loaded solvent is then stripped by adding ammonia, and APT is subsequently obtained. During solvent extraction, kerosene and decanol are usually introduced as the diluent and modifier, respectively. A 201×7 gel anion ion-exchange resin was used during the ion exchange to replace the solvent exchange step to improve the tungsten recovery rate. Using an anion exchanger for tungsten recovery from a water-based solution, impurity ions, such as AsO_4^{3-}, PO_4^{3-}, and SiO_3^{2-}, can be separated from WO_4^{2-} since the adsorption affinities of different anions are different. Anion exchange membranes are also a frequently applied technology [32,33].

A fully innovative process from the mineral to the product is usually rather difficult for a company to adopt, even though it may fulfill the principles cleaner production. As a compromise, partial optimization or innovation is sometimes more effective than the modification of the whole process.

Table S2

Industrial pollution discharge and emissions of China's smelting and processing of non-ferrous metals industry during the period of 2011-2015.

Year	Industrial wastewater (thousand tons)			Industrial emissions (thousand tons)			
	Wastewater (million tons)	COD	Ammoniacal nitrogen	Exhaust gases (billion m3)	SO_2	NO_x	Smoke dust
2011	335	29.7	18.7	3189	1146	202	348
2012	288	27.8	15.5	3180	1144	230	319

2013	276	28.3	12.8	3263	1223	264	360
2014	310	29.0	12.1	3617	1230	328	385
2015	321	30.6	9.6	3981	1209	327	391

Data origin: China Statistical Yearbook on Environment (2012-2016)

The cost effectiveness was normalized relative to the cost of P1, and each step of the whole process was individually taken into account. In an APT production company, the environmental risk during APT production is usually due to waste generation. For example, in traditional processes, severe waste gas emission occurs along with the generation of wastewater containing ammonia and heavy metals. Using the WPPC concept, it is expected that the environmental impacts can be reduced, and a cleaner production of APT can be achieved.

Table S3

Composition of the scheelite concentrate

Elements	WO3	Ca	Fe	Mn	S	As/ppm	Ni/ppm
wt.%	53.18	21.79	0.22	0.07	0.55	241	37
Elements	Zn/ppm	Mo	Pb/ppm	Cd/ppm			
wt.%	302	0.47	177	5			

Composition of the mixture of the leaching residue and the residue from impurities removal

Elements	WO3	Ca	Fe	Mn	S	As/ppm	Ni/ppm
wt.%	3.23	26.11	0.12	0.03	0.55	363	10
Elements	Zn/ppm	Mo	Pb/ppm	Cd/ppm			
wt.%	202	0.07	271	-			

Composition of the solution before disposal for waste water treatment

Elements	WO3	Mo	P	As	Ni	Cl-	N(NH3-N)
g/l	0.48	0.039	0.77	0.01	0.01	0.42	1.65

Table S4

Raw data for cost calculations

		Water, t	Electricity, kwh	Natural gas, m^3	Steam, t	Mineral, t (cost excluded)	Chemicals, t	Waste gas, m^3	Solid waste, t	Waste water, t
		Extraction step								
PI	**raw data**	4.45±0.15	1016±17	50±6	1.56±0.79	1.425±0.132	0.1±0.07	6.25±0.33	1.98±0.16	0
	unit cost, cny	*0.95*	*0.83*	*4.6*	*200*	*73000*	*2500*	*3.48*	*1000**	
	cost/t APT, cny	8.9	843.3	153.1	280.8	99750	250	21.74	1985.65	
							1536			
PII	raw data	45±9	300±23	0	2±0.33	1.396±0.046	0.98±0.21	0.40±0.29	1.32±0.18	0
	cost/t APT, cny	90	249.01		360	97720	2450	1.39	1320	
							3149			
PIII	raw data	50±5	302±14	0	1.9±0.15	1.386±0.037	0.99±0.15	0.42±0.07	1.32±0.09	
	cost/t APT, cny	100	250.66		360	97020	2475	1.46	1320	0
							3159			
		Purification step								
		Water, t	Electricity, kwh		Steam, t		Chemicals, t	Waste gas, m^3	Solid waste, t	Waste water, t
PI	**raw data**	28.6±0.7	653.6±31		1.56±0.25		0.1±0.0	3.23±0.16	0.0175±0.007	
	unit cost, cny	*0.95*	*0.83*		*200*		*2500*	*3.48*	*1000*	
	cost/t APT, cny	57.2	542.5		280.8		250	11.23	17.52	
							1130.5			
PII	raw data	40±6	90±12		0		0.7±0.22	0	0.164±0.058	
	cost/t APT, cny	80	74.70				1750		164	
							1904.702			
PIII	raw data	20±8	100±14		0		0.5±0.17	0	0.07±0.02	
	cost/t APT, cny	40	83.01				1250		70.09	
							1373.002			
		Product step								
		Water, t	Electricity, kwh		Steam, t		Chemicals, t	Waste gas, m^3	Solid waste, t	Waste water, t
PI	**raw data**	3.65±0.27	326.6±4.3		3.13±0.61		0	8.5±0.32	-	8±1.5
	unit cost, cny	*0.95*	*0.83*		*200*		*2500*	*3.48*	*1000*	*2.39*
	cost/t APT, cny	7.3	271.1		563.4		0	29.60		19.16
							841.8			**2084.9**
PII	raw data	1.99±0.14	110±19(18.91)		2.5±0.3		0	17.6±0.8		167±21
	cost/t APT, cny	4	91.31		450		0	61.25		400
							545.3074			**2040.5**
PIII	raw data	5±0.09	107±23		2.6±0.6		0	0		75±9
	cost/t APT, cny	4	88.81		450		0			179.641
							545.3074			**1565**

**landfilling cost; USD/CNY=6.93; data obtained via continuous operation for half year and unit cost is local cost in Jiangxi province in China.*